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LXXXV. *Interference Calculations and Wave Groups* \*.  
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*Summary.*

THE full scope of interference calculations depends on the utilization of *physically non-real* wave components. The Saddle Point Method is truly a stationary phase calculation in that it emphasizes a set of damped waves of constant phase, while the Kelvin (Stationary Phase) Method is shown to really imply constancy of amplitude for the interfering wavelets. On the basis of this last remark the Kelvin Method is extended to cases where the orthodox formulation would be inaccurate. For the canonical form corresponding to the most general statement of the Steepest Descent scheme the Kelvin Method yields a Fourier Integral. The concept of group velocity for non-linear argument functions of  $x, t$  may be extended in two different ways denoted by  $U_1$  and  $U_2$ . Errors are pointed out in the contribution of Green to this subject. A theorem due to Havelock is proved in an alternative manner and

\* The most extensive contemporaneous work on wave groups is probably that of de Broglie. The results mentioned here are not in the line of his researches.

† Communicated by the Author.

certain generalizations indicated, including the case of media with potential energies of type

$$\sum_{i,j}^n a_{ij} \frac{\partial^i y}{\partial x^i} \frac{\partial^j y}{\partial x^j}; \quad i+j \text{ even and } a_{ij} = a_{ji}.$$

It is demonstrated that each component energy travels with the group velocity of the sum. A tentative theorem suggested by Tonks is shown to be inadequate in general, and in the corrected form, for a particular class of dynamical media, to be a paraphrasing of the Havelock theorem. A special class of media involving energy sources (sinks) is taken up, and it is shown that mathematically equivalent forms of the defining differential equation are associated with altogether different types of physical systems, even though the character of the wave propagation is not affected. The scope of the theorem about energy propagation with group velocity is further extended by showing that for the dissipative medium instanced, and for the media with equivalent mathematical representations, the energy is propagated with the generalized group velocity. In the proof the method of Ferrari is generalized to apply to dissipative media. Finally, the difficulties involved in employing physically meaningful series representations, such as suggested by Flamm for wave packets, are pointed out.

**I**T is, perhaps, superfluous to remark the increasing employment of the concepts of interference and group velocity in modern theories of physics and, indeed, their use as guides for the developments of pure mathematics. It seems timely, therefore, to present some extensions and generalizations having to do with both of these topics as well as a critique of some of the published work bearing on this field. The preceding summary lists the particular questions taken up.

In a wide range of problems of mathematical physics one of the classical solutions is the definite integral type

$$y(x, t) = \int_{\text{real path}} K(x, t; k) \phi(k) dk, \quad . . . \quad (1.00)$$

where the kernel very often is an entire function in  $k=u+\sqrt{-1}v$ , satisfying certain symmetry conditions

in  $x$  and  $t$ . The discussion will be restricted to the Cauchy problem for partial differential equations of wave type. In such cases the kernel will represent a wave and the integral, as a whole, the superposition of an infinitude of waves differentiated in value of the parameter  $k$ . This, then, is a resolution of the associated physical phenomenon, but other resolutions amounting mathematically to allowable deformation of the contour may easily be given according to the scheme

$$u=f_1(v), \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (1.01)$$

$$u=f_2(v; x, t). \quad \dots \quad \dots \quad \dots \quad \dots \quad (1.02)$$

The physical interpretation of eq. (1.01) is the replacement of one set of components by an equivalent set also capable of propagation in the medium, though governed by a different relation of phase to damping. More particularly, the new integrand of eq. (1.00) obviously remains a solution of the defining differential equation. In general, however, the substitution of eq. (1.02), although yielding equivalent mathematical representations, does not give an alternative physically descriptive wave system, because the component waves (*i. e.*, the new integrand) are no longer compatible with the differential equations of the medium.

A central problem is that of approximating the superposition or interference of waves implied in eq. (1.00) by fixing on a component wave set, such that the contributions to the resultant disturbance outside a small range of frequencies are negligible. From what has been said in connexion with the transformation eq. (1.02), it is clear that a specialization of the interference principle to waves satisfying the condition of physical reality for the medium would considerably hamper the application of mathematical methods.

The Kelvin-Rayleigh Stationary Phase Principle \* is one such method of approximation, and considers only constructively interfering simple sinusoidal waves in the neighbourhood of a dominant phase. The nomenclature Stationary Phase Principle seems to the writer to be somewhat misleading, for it is more exactly characterized in the large as a stationary amplitude calculation. In a physical sense it considers the superposition of a group of wavelets of phases varying slightly around the

\* Lord Kelvin, Proc. Roy. Soc. xlvi. p. 30 (1887).

dominant phase and of fixed amplitude for the components. A real stationary phase principle is that referred to as the Saddle Point Method \*, or method of Steepest Descent. The relationship of both these methods, the wave implication of the latter and the true understanding and generalization of the former, constitutes the novelty of the first section of this paper.

The wave integrals to be considered now are mostly of the form

$$\int e^{j\psi(k; x, t)} dk, \quad j = \sqrt{-1}, \quad (1.011)$$

and usually either the real or imaginary parts are of eventual interest.

One recalls that the *raison d'être* of the Saddle Point Method is the use of contours † which pass through a min.-max. or saddle point (or col) (*i. e.*, a  $k$  value for which  $\frac{d}{dk} \psi(k; x, t) = 0$ ) of the integrand. Assuming analyticity in the neighbourhood of the saddle point, it follows that the direction of most rapid decrease of the real part is along a contour determined by the condition that the imaginary part be constantly equal to its value at the saddle point. If the rate of decrease is large enough, it suffices to take the first few terms of a series expansion and to integrate this approximating function along the whole contour to arrive at a close estimate. In a physical sense, by keeping the imaginary part fixed, one sums up a group of constructively interfering damped waves of constant phase and varying amplitude, thus justifying reference to this method as a true stationary phase calculation ‡. Now even when the saddle point is on

\* Watson, 'Bessel Functions,' p. 235.

† These contours end up, of course, either in poles, essential singularities or at infinity. Several saddle points may be present on one contour, but in such a case all except one are inflexion points for the real part of the function expressed in terms of the path parameter. Physically speaking, only the one wave group characterizes the disturbance in this instance. If, however, these various saddle points are on different branches joining at infinity, then the physical meaning is that of several wave groups concerned in the phenomenon.

‡ A graphical demonstration of the physical alternatives is afforded by representing a set of waves differing in phase though of uniform amplitude by a circle of radius equal to this amplitude. If now the angular density of the components be indicated by the number of radii drawn in the interval  $\theta$  to  $\theta + \Delta\theta$ , it will be apparent that the one-method approximates by summing the projections of the amplitudes on the radius vector drawn at the angle associated with maximum concentration, whereas the other sums along that part of the circumference in the immediate neighbourhood of this radius.

the real axis, the orthodox Stationary Phase Method may yield poor approximations. This is because, in contradistinction to the variety allowed by the Steepest Descent Method, it involves always a straight line (namely the real axis) for the integration path. If the saddle point be off the real axis, the Stationary Phase Principle is generally inapplicable and the approximation suggested may be very bad indeed, except when the amplitude factor has a maximum for the value of  $x$  and  $t$  characterizing the dominant phase \*.

As a guide to a generalization of the Kelvin Method, the following example is adduced. Though the min.-max. lies on the real axis, the approximation by the Standard Stationary Phase Evaluation is poor.

Ex. (1).

$$\text{R.P. } \int_{-\infty}^{\infty} e^{j\{k^2t(\beta^2-1)-kx(\beta^2-1)+\beta^2x^2/4t\}+2\beta(k-x/2t)^2t+j \operatorname{arc} \tan \beta} dk. \quad \dots \quad (1.03)$$

\* For

$$\text{R.P. } \int_{\infty}^{\infty} e^{-k^2t+j(kx-k^2t)} dk. \quad \dots \quad (a)$$

the saddle point is  $k_0 = (1+j)x/4t$  which, neglecting exceptional values of  $x$  and  $t$ , is off the real axis. The two possible paths are

$$u = \alpha_i v + \beta_i \quad \left. \begin{array}{l} \alpha_i = (-1)^{i+1} \sqrt{2} - 1, \quad \beta_i = \{(-1)^i \sqrt{2} + 2\}/4, \quad i=1, 2, \end{array} \right\} \quad (b)$$

for a convergent integral the signs for  $i=2$  are to be taken with

$$dk = \exp \operatorname{arc} \tan (-(1+\sqrt{2})^{-1}) dv.$$

Eq. (a) reduces to

$$\text{R.P. } e^{-(x^2/8t)+jx^2/8t} \int_{-\infty}^{\infty} e^{-i\alpha_2(v-x/4t)^2} dv.$$

Since

$$\operatorname{arc} \tan (-/1\sqrt{2}+1)^{-1} = -\pi/8; \quad \frac{1}{2}[(\alpha_2^2+1)/\alpha_2]^{1/2} = 2^{1/4},$$

the final result is

$$(\pi/\sqrt{2}t)^{1/2} e^{-x^2/8t} \cos(x^2/8t - \pi/8).$$

The Stationary Phase Principle is summarized in the formula

$$\left[ t \frac{dU(k)}{dk} \Big|_{k_0} \right]^{1/2} \phi(k_0) \cos k_0 \left( x - V(k_0)t \mp \frac{\pi}{4} \right)$$

(Havelock, Cambridge Tract, 'Propagation of Disturbances in Dispersive Media').

As expected, it is almost valueless here. The approximation derived from it is

$$(2\pi/t)^{1/2} e^{-x^2/4t} \cos(x^2/4t - \pi/4),$$

which differs markedly from the exact value.

If the complex  $k$  plane be rotated about the saddle point

$$k_0 = \frac{x}{2t}, \text{ i.e., } \bar{k} = k + j \left( k - \frac{x}{2t} \right) \beta,$$

the integral is easily shown to merge into

$$\text{R.P.} \quad (1+\beta^2)^{-1/2} \int_{-\infty}^{\infty} e^{jk(x-\bar{k}t)} dk, \quad \dots \quad (1.031)$$

which is evaluated rigorously for  $t > 0$  as

$$\left( \frac{\pi}{t(1+\beta^2)} \right)^{1/2} \cos \left( \frac{x^2}{4t} - \frac{\pi}{4} \right). \quad \dots \quad (1.032)$$

Direct application of the Kelvin Method gives

$$(1+\beta^2)^{1/2} \left( \frac{\pi}{t(1-\beta^2)} \right)^{1/2} \sin \left( \frac{x^2}{4t} + \frac{\pi}{4} + \arctan \beta \right). \quad (1.033)$$

The "best" contour for the applicability of the Kelvin Method is found by comparing eq. (1.033) with the accurate solution eq. (1.032). Evidently the steepest descent contours, namely, those for which  $\beta = -1$  are *worst* for the Kelvin case, and exact correspondence is obtained only for  $\beta = 0$ . In this latter case the amplitude is invariable and equal to unity.

It thus appears that not only is the nexus of the Stationary Phase Method the use of a contour on which the amplitude function is constant, but that the Stationary Phase scheme may be immediately extended to the case where the saddle point lies off the real axis—in short, having found the saddle point, one employs here the paths along which the amplitude is constant in contradistinction to the procedure of the Steepest Descent calculation, which depends on constant phase paths. Thus the generalized Stationary Phase paths for  $\exp. \psi(k; x, t)$  are the steepest descent paths for  $\exp j\psi(k; x, t)$ . The constant phase and constant amplitude contours are, of course, generally orthogonal except at the critical points where the contours of one set bisect the angles between the contours of the other.

From the viewpoint of integration in the complex plane, since the steepest descent and generalized Kelvin methods are related in the sense of furnishing two of the infinitude of possible deformations of an original contour, evidently the results must be the same. This presupposes that both are permissible contours\*. The

\* It is, of course, always necessary to demonstrate the allowability of the deformed path. In general contours at infinity are required to give a closed curve. If polar singularities are encountered in the

examples given above are special cases of the second degree polynomial  $\dagger$  as exponent  $\ddagger$ —here both methods

deformation the usual residues must be added. In example 1,  $\beta = -1$ , the negative and positive parallels to the imaginary axis are the connecting paths at the eastern ( $+\infty$ ) and western horizons. For  $t > 0$  it is at once established that the integrals along these lines are 0.

$\ddagger$  Let the integral be

$$\text{R.P. } \int_{-\infty}^{\beta} e^{f(k; x, t)} dk = \int_{-\infty}^{\beta} e^{f(k_0) + f'(k-k_0) + \frac{f''(k-k_0)^2}{2!}} dk,$$

where higher order terms are neglected in the approximation to  $f(k)$ , and  $\alpha$  and  $\beta$  are real limits which may be taken here as 0,  $\infty$  or  $-\infty, \infty$ . The generalized Kelvin Method will be applied to this typical case.

There is only one saddle point found as usual by setting  $f'(k)=0$ . Formally then

$$\begin{aligned} \text{R.P. } & e^{f(k_0)} \int_{-\infty}^{\beta} e^{f''(k_0)(k-k_0)^2/2} dk \\ &= ae^{f(k_0)} \int_0^{\infty} e^{\frac{|R_{\mu\mu}|_0 + jI_{\mu\mu}|_0}{2} + \rho^2 e^{j(2\theta + \text{arc tan } \frac{I_{\mu\mu}}{R_{\mu\mu}}|_0)}} d\rho, \end{aligned}$$

where  $f = R + jI$  and  $\frac{I_{\mu\mu}}{R_{\mu\mu}}|_0 = - \lim_{k \rightarrow k_0} \frac{R_v}{R_u}$

and  $a=1$  or 2 according as  $\alpha=0$  or  $-\infty$ . If this is to be a constant amplitude contour,

$$2\theta + \text{arc tan } \frac{I_{\mu\mu}}{R_{\mu\mu}}|_0 = +\frac{\pi}{2},$$

therefore there results

$$\begin{aligned} ae^{f(k_0) + j[-(\text{arc tan } \frac{I_{\mu\mu}}{R_{\mu\mu}}|_0 + \frac{\pi}{2})/2]} \int_0^{\infty} e^{+j|f''(k_0)|\rho^2/2} \\ + \text{connecting integrals.} \end{aligned}$$

Suppose, as usual, that the connecting integrals are 0, then the end result is

$$\text{R.P. } \frac{1}{2}a[2\pi/|f''(k_0)|]^{1/2} e^{R(k_0) + j[\frac{\pi}{2} - \frac{1}{2}\text{arc tan } \frac{I_{\mu\mu}}{R_{\mu\mu}}|_0 + I_0]}.$$

It is to be borne in mind that for the existence of the original integral between the limits  $-\infty, \infty$  a sufficient condition is  $R_{\mu\mu}|_0 < 0$ . If  $R_{\mu\mu}(k_0)=0$  the integral between  $-\infty, \infty$  diverges, though the integral  $v, \infty$  may exist if  $R(k_0) > 0$ . Of course, in this latter case a connecting contour to any point on the deformed contour from 0, 0 will, in general, carry a non-zero contribution and may be selected as a constant amplitude or constant phase path.

$\ddagger$  Very recently the writer has become acquainted with the lucid geometric picturization of the saddle point method in Jeffreys—‘Operational Methods in Mathematical Physics.’ His remarks (top of p. 80, for instance) about the two saddle points on the one steepest descent path may be misleading to the reader—evidently the curve goes to  $\infty$  between the saddle points (i.e.,  $u \rightarrow 0$ )  $|v| \rightarrow \infty$ ). The results for water waves seem to the writer not wholly complete, for the presence of the enumerable infinitude of essential singularities on the negative axis requires that proof be given that the value of the integral may be obtained from the simple steepest descent contour and exponent used for approximation.

are equally efficacious. The use of the quadratic exponent generally implies approximations to *both* the exponent and the true path. The last observation indicates that approximations to the steepest descent or constant amplitude paths, accurate in the effective neighbourhood of the saddle point, may be used in the extension of the method to more complicated exponents.

In point of fact, the details of calculation for the saddle point method given in ex. 1 (*cf.* also footnotes \* and † on pp. 1037 and 1039) are not typical of the treatments generally presented. The more usual procedure for

$$\int e^{\psi(k; x, t)} \phi(k) dk$$

is, essentially, to write

$$\left. \begin{aligned} \omega &= \psi^{(k; x, t)}, \\ \omega_0 &= \psi^{(k_0; x, t)}, \end{aligned} \right\}$$

where  $k_0$  is the saddle point. Next it is observed that for the steepest descent contour  $u - u_0 \rightarrow -\infty$  on either side of the saddle point, while  $v - v_0 \equiv 0$ . Accordingly the integrand is written in canonical form as

$$e^{\omega_0} \int_0^{-\infty} e^{\bar{u}} \left\{ \left( \phi(\bar{u}) \frac{dk}{d\bar{u}} \right) \Big|_1 - \left( \phi(\bar{u}) \frac{dk}{d\bar{u}} \right) \Big|_2 \right\} d\bar{u}, \quad \bar{u} = u - u_0, \quad \dots \quad (\text{A})$$

where the subscripts distinguish the two branches leading from the col point. In general the multiplier of the exponential for the non-trivial case is a multiform function of  $w$ , and the branch in question is chosen by the condition that  $\bar{u}$  be positive real on the path. Evidently this method applied to ex. (1) and footnotes \* and † on pp. 1037 and 1039 yields with equal ease the closed form found in the text. The general case associates an infinite series \*.

Suppose now that the generalized Kelvin Method were used, then, *pari passu*, the canonical form † would be

$$e^{\omega_0} \int_0^{-\infty} e^{\bar{v}} \left\{ \left( \phi(\bar{v}) \frac{dk}{d\bar{v}} \right) \Big|_1 - \left( \phi(\bar{v}) \frac{dk}{d\bar{v}} \right) \Big|_2 \right\} d\bar{v}. \quad (\text{B})$$

\* The series is in integral powers of  $\omega^{1/r}$ , where  $r > 1$  is integral.

The individual term integrals are of type  $\int_0^\infty u^q e^{-u} du$ , which is at once

recognized as the  $F$  function integral.

† However, the simplicity of the group of waves interpretation is sacrificed by this type of canonical resolution.

This is recognized immediately as a Fourier integral \*. The series expansion of the exponential multiplier, which under broad conditions is integrated to give asymptotic series, is here inapplicable because of the divergence of the individual integrals, though either summability methods or the Sommerfeld factors, etc., are available to increase the class of meaningful integrals. Accordingly, assuming  $B$  is convergent, its calculation depends on expanding  $\left( \phi(\bar{v}) \frac{dk}{d\bar{v}} \right) \Big|_2^1$  in a suitable series whose term

by term integrated products with the exponential exist.

Clearly the scope in the sense of easily demonstrated convergence properties and the relatively compact integrand range of importance are by themselves sufficient to single out the steepest descent contours. The generalized Kelvin contours from the canonical form of the last paragraph deserve consideration above the other alternative paths because of the practical convenience attendant upon the existence of extensive tabulations of Fourier transforms †. Besides, it may happen, because of the existence of branch cuts, that only the  $B$  paths are allowable "simple" deformations.

We turn now to another topic, namely, the nature of the group velocity. For the definition of group velocity the usual corpus for the phase term is

$$k(x - V(k)t) = f(k; x, t). \dots \quad (2.00)$$

A different type of phase expression has been considered by Green ‡, namely, the one case

$$\frac{x^2 t}{\mu(1+t^2)} = J(x, t).$$

His method consists in determining a wave-length by a condition

$$J(x+\lambda, t) - J(x, t) = 2\pi, \dots \quad (2.01)$$

and the group velocity is obtained from this implicit relation as

$$\frac{dx}{dt} = U. \dots \quad (2.02)$$

\* Even had the original integral been a Fourier integral, this is in general a different one because of the path change.

† Campbell and Foster, Fourier Int. for Practical Use.

‡ G. Green, Proc. Roy. Soc. Edinburgh, xxix. p. 393 (1908).

Green's treatment is not in accord with the extensions to the case of a general phase function  $F(x, t; k)$  to be developed in this section, and a criticism of his work is given below\*.

Attention ought to be given to the necessity of precision in stating the problem. One may consider the phase term of the resultant wave in which there is no longer an arbitrary parameter, *i.e.*,

$$F(\bar{k}(x, t); x, t) = J(x, t)$$

and define a group velocity  $U_1$  of the original components with phase terms as in eq. 2.00), or,  $U_2$ , one may treat the propagation of a group each of whose components

is of type  $\frac{\sin}{\cos} F(k; x, t)$  with varying  $k$ . It will appear

\* That Green's procedure is unsatisfactory appears already from eq. (2.051), which yields a result differing from that of eq. (2.01).

For instance, with  $V(k)=k$ ,  $J(x, t)=\frac{x^2}{4t}+C$ ; his mode of calculation (eq. (2.01) results in the quadratic  $2\lambda x + \lambda^2 = 2\pi t$  for  $\lambda$  rather than the known value  $\lambda=\pi t/x$ . The situation is even worse for eq. (2.081), where simple dimensional considerations show that the parameter  $\lambda=2\pi/k$  is no longer a wave-length. With  $F(k; x, t)=k(x^2-kt)$  the argument of the sine term in the resultant, assuming, as usual, a superposition given by

$$\int \phi(\lambda) e^{j \frac{2\pi}{\lambda} (x^2 - \frac{2\pi}{\lambda} t)} d\lambda.$$

is, except for a phase constant,  $\frac{x^4}{4t}$ , and

$$k_0 = 2\pi/\lambda_0 = x^2/2t.$$

Eq. (2.01) gives a fourth degree equation for  $\lambda$ , whose roots are completely out of accord with the correct value just given. Even the emendation  $\frac{\partial}{\partial x}(x^4/4t)=x^3/t$  is useless here. Furthermore, even if we were to correct Green's method by substituting eq. (2.051), Green's example, since it belongs to the category connected with  $U_2$ , would still be outside the scope of validity of the formula (for evidently  $x^2t/\mu(1+t^2)$  does not satisfy the necessary condition eq. (2.05)). At first sight Green's result that the group velocity and wave velocity are related in the correct way, 2 : 1, for flexural waves seems to lend some post hoc justification to his method of calculation—however, reference to his paper discloses the fact that the complete phase argument is

$$x^2t/\mu(1+t^2) - \frac{1}{2} \arctan t.$$

When  $t$  is large, this last term is practically constant ( $= \frac{\pi}{4}$ ), but then the first term is essentially  $x^2/t$ , which is of the proper form and is amenable to eq. (2.051). When  $x$  and  $t$  are small, the variation in the  $\arctan t$  term cannot be neglected, and the calculation by the Green method must give at best

$$U/V = 2x(1-t^2)/[x(1-t^2) - \beta(1+t^2)]$$

and not 2.

that the two group velocities, or perhaps more felicitously the velocities of the two group types thus defined, generally differ in value.

Consistent determinations of  $U_1$  and  $U_2$  may be given rather simply. Consider  $U_1$  first. It is necessary primus, to determine the condition that  $J(x, t)$  arise from a superposition of sinusoidal waves with arguments linear in the variables. In this case a transformation of parameter will reduce the phase to the canonical form  $k(x - V(k)t)$ . Evidently  $U_1$  is always  $x/t$ . The dominant  $k$  values denoted by  $k_i$ ,  $i=1, \dots, n$  (where  $n$  represents the number of roots of eq. 2.03) are derived from

$$\frac{d}{dk} kV(k) = x/t. \quad \dots \quad (2.03)$$

Thus

$$J_i(x, t) = F_i\left(k_i\left(\frac{x}{t}\right); x, t\right) = \bar{k}_i(x, t)(x - V\bar{k}_i(x, t)t). \quad (2.04)$$

on substituting the stationary value of  $k_i$  appropriate to  $x$  and  $t$ .

From eq. (2.03),  $k_i$  must be of the form  $k_i\left(\frac{x}{t}\right)$ , therefore

$$J_i(x, t) = \bar{k}_i\left(\frac{x}{t}\right) \left\{ x - V_i\left(\frac{x}{t}\right)t \right\} = tN_i\left(\frac{x}{t}\right). \quad (2.05)$$

Conversely

$$\begin{aligned} \frac{\partial}{\partial x} tN_i\left(\frac{x}{t}\right) &= \left( \frac{\partial}{\partial x} + \frac{\partial k}{\partial x} \frac{\partial}{\partial k} \right) k(x - V(k)t) \Big|_{k=k_i} \\ &= k_i + \left( x \frac{\partial k}{\partial x} - \frac{\partial k}{\partial k} \frac{\partial V(k)}{\partial x} t \right) \Big|_{k=k_i} \end{aligned}$$

eq. (2.03) shows that the last two terms cancel and there results

$$\frac{\partial}{\partial x} tN_i\left(\frac{x}{t}\right) = k_i. \quad \dots \quad (2.051)$$

Moreover,

$$-\frac{\partial}{\partial x} \frac{\partial}{\partial t} tN_i\left(\frac{x}{t}\right) = -\frac{\partial k_i}{\partial t} = U_1; \quad \frac{x}{t} \quad . \quad (2.052)$$

as is verified by reference to eq. (2.08).

Eq. 2.05 is a necessary consequence of the phase type for the individual components. To investigate sufficiency,

one observes that given  $J(x, t) \equiv tN\left(\frac{x}{t}\right)$ ,

$$k(u) = \frac{dN(u)}{du}, \quad \dots \dots \dots \quad (2.051)$$

$$V(u) = u - N(u) \Big/ \frac{dN(u)}{du}; \quad u = \frac{x}{t} \quad \dots \quad (2.053)$$

Hence generally  $k$  and  $V$  are determined uniquely as functions of  $x/t$ , and the inversion (usually not unique) of eq. 2.051 fixes  $V$  in terms of  $k$ .

So far as the formal determination of  $U_2$  is concerned, no such restriction as that of eq. 2.05 for the phase function type is necessary. Consider, then, the general phase argument  $F(k; x, t)$ . The components combining for constructive interference are characterized by values of  $k$  for which

$$F_k = \frac{\partial}{\partial k} F(k; x, t) = 0. \quad \dots \quad (2.06)$$

Each solution  $k_i$  of eq. 2.06 is correlated with a different group velocity defined by the condition that

$$(dk_i)_{U_2=U_2(k_i)} = 0. \quad \dots \quad (2.07)$$

On dropping the subscript on  $k$ , one may write

$$\frac{dx}{dt} = U(k) = -\frac{\partial k}{\partial t} \Big/ \frac{\partial k}{\partial x}. \quad \dots \quad (2.08)$$

From eq. (2.06) one derives.

$$\left. \begin{aligned} \frac{\partial F_k}{\partial x} + F_{kk} \frac{\partial k}{\partial x} &= 0, \\ \frac{\partial F_k}{\partial t} + F_{kk} \frac{\partial k}{\partial t} &= 0. \end{aligned} \right\} \quad \dots \quad (2.061)$$

Thus in the case that \*  $F_{kk} \neq 0$

$$U_2(k_i) = -F_{kt}/F_{kx}|_{k_i}. \quad \dots \quad (2.081)$$

\* Assuming  $F$  really contains  $k$ , the case  $F_{kk}=0$  corresponds to (a) a linear dependence of  $F$  on  $k$ , or (b) a multiple root of eq. (2.06). In the latter case successive differentiation gives for  $F_{kn}(k_i; x, t) \neq 0$ ,

$$U_2 = -F_{kn-1,t}/F_{kn-1,x}.$$

It is easy to verify that eq. (2.081) is consistent with the usual results when  $F = k(x - V(k)t)$ . Moreover, it will be shown later that the velocity of energy propagation in a more general case than that heretofore considered is given by  $U_2$ . It needs to be pointed out that in the final result eq. (2.081) or eq. (2.082),  $k$  is to be replaced by its value in terms of  $x$  and  $t$  as found from eq. (2.06). With this understanding it may be shown that  $U_2$  is independent of change in the parameter. For if  $k = \Pi(w)$  for a map of the whole real axis on itself ( $\Pi(w)$  cannot be  $\sin w$ , for instance, if we restrict our discussion to real parameter values)

$$U_2' = \frac{F_{wt}}{F_{wx}} = \frac{(F_k k_w)_t}{(F_k k_w)_x} \dots \dots \quad (2.083)$$

For these partial derivatives  $k$  is considered independent of  $x$  and  $t$ , hence  $k_w$  may be taken outside the brackets, and therefore

$$U_2' = U_2,$$

where  $w$  is to be replaced by the value  $\bar{w}(x, t)$  a solution of

$$F_w = F_k \frac{\partial \Pi(w)}{\partial w} = 0. \dots \dots \quad (2.09)$$

The roots of  $\frac{\partial \Pi(w)}{\partial \bar{w}} = 0$  are independent of  $x$  and  $t$  and are, of course, neglected. The pertinent values of  $w_i$  are given by

$$\Pi(w_i) = k_i(x, t),$$

so that it has been demonstrated that, except for differences in multiplicities of corresponding parameter values, there are the same number and values of discrete wave group velocities.

Before leaving this topic it may not be amiss to point out explicitly that in all cases where the amplitude factor involves  $k$  as well as  $x$  or  $t$ ,  $U$  is complex. Except in the case of potential barrier leakage in quantum theory where they cannot be escaped, complex group velocities have not been given much attention. If the amplitude factor is independent of  $k$  then only the phase velocity is complex.

The next chapter treats the propagation of energy with group velocity. Various special cases are mentioned in

the literature, and Havelock states a fairly general theorem which includes many of these particular examples for media whose energy densities are expressible in the form

$\sum a_i \left( \frac{\partial^i y}{\partial x^i} \right)^2$ . Havelock's proof \* consists in actually computing the mean energy transfer velocity in terms of a ratio of two series in the frequency, and showing that this ratio is  $\frac{d}{dk} kV(k)$  in the notation of this paper †. The

proof leaves open the question as to whether each type of energy is carried on at its own velocity and the transfer found is a mean velocity, or whether each component energy is advanced at the same average rate. The following proof indicates the latter is true, and serves to characterize easily a number of extensions of Havelock's theorem.

It is plain that the Havelock media support the wave function  $\cos k(x - V(k)t)$ . Interest lies in the propagation of energy of frequency  $k$ . Accordingly a simple group is written as

$$y = R.P. \int_{-\infty}^{\infty} C(k) e^{jk(x - V(k)t)} dk, \dots \quad (3.00)$$

where  $|C(k)|$  is practically 0 outside the range  $k_0 \pm \epsilon$  and slowly varying for  $|k - k_0| < \eta \leq \epsilon$ . Havelock uses the integral with limits  $k_0 \pm \eta$ , and neglects quadratic terms in  $k$  for the exponent. It is these neglected terms, however, that carry the damping factor, and one misses the nature of the restrictions on  $t$  and  $\eta$  required for

\* Havelock uses his eq. (81) (*loc. cit.*) as a plausibility argument for the single case: energy  $\sim y^2$ , but his method is to consider a stationary observer and to average over values of  $t$  alone (constant  $x$ ). This leaves the result somewhat in doubt. For one thing it is necessary to assume that  $f(x - U_0(t + t_1))$ ,  $t_1$  a period, differs only slightly from  $f(x - U_0 t)$  and leaves undetermined the way the group actually moves on.

† Surprisingly enough, in spite of the incontestability of Havelock's proofs, his statement is incorrect for this theorem as well as for all the other cases treated in his chapter vi., *loc. cit.* (*i.e.*, pp. 57-60, 62, 64, and 65). What has actually been shown in our paper, as well as in Havelock's book, is that the *mean energy* is propagated with group velocity, whereas Havelock's statements are uniformly to the effect that the *mean velocity* of energy propagation is  $U$ . The distinction is that between a ratio of two mean values and the mean value of the ratio.

validity of the theorem, cf. eq. (3.012).  $U_0 = \frac{d}{dk} kV(k) \Big|_{k_0}$

is the group velocity for  $k_0$  which, of course, need not be the saddle-point value, and we will assume  $\frac{\partial U}{\partial k} \Big|_{k_0} \equiv U'_0$

is large compared to all succeeding terms in the expansion of  $kV(k)t$  for moderate values of  $k - k_0$  (say such that  $|k - k_0| < \epsilon$ ). One finds for the prototype,  $C(k) = e^{-\rho(k-k_0)^2}$ ,

$$\frac{\partial^n y}{\partial x^n} = R.P. j^n e^{jk_0(x - V(k_0)t)} \int_{-\infty}^{\infty} (z + k_0)^n e^{-(\frac{1}{4}tU'_0j + \rho)z^2 + j(x - U_0t)z} dz, \quad \dots \quad (3.01)$$

$$y = \rho^{-1/2} \left\{ \pi^2/1 + \left( \frac{tU'_0}{2\rho} \right)^2 \right\}^{1/4} \\ \times \exp - \left[ (x - U_0t)^2/4\rho \left( 1 + \left( \frac{tU'_0}{2\rho} \right)^2 \right) \right] \\ \times \cos \left[ k_0(x - V_0't) + \frac{(x - U_0t)^2}{2(tU'_0 + 4\rho^2/tU'_0)} - 1/2 \arctan \frac{tU'_0}{\rho} \right].$$

$\frac{\partial^n y}{\partial x_n}$  contains R.P. and J.P.  $\left( \frac{x - U_0t}{2\rho + tU'_0 j} \right)^2$ ,  $r \leq n$ , as multipliers of the original ( $y$ ) amplitude. For  $y'$  we have, for instance,

$$-\frac{\partial \tilde{y}}{\partial x} = k_0 \tilde{y} + \frac{x - U_0t}{2\rho^{3/2}} \frac{\pi^{1/2}}{[1 + (tU'_0/2\rho)^2]^{3/4}} \\ \times \exp - \left[ (x - U_0t)^2/4\rho \left( 1 + \left( \frac{tU'_0}{\rho} \right)^2 \right) \right] \\ \times \cos \left[ k_0(x - V_0't) + \frac{(x - U_0t)^2}{2(tU'_0 + 4\rho^2/tU'_0)} - \frac{3}{2} \arctan \frac{tU'_0}{\rho} \right]. \quad \dots \quad (3.011)$$

$\tilde{y}$  is the J.P. of the integral of eq. 3.00.

For

$$t \ll \frac{\rho}{U'_0}, \quad \dots \quad (3.012)$$

the formulæ reduce to

$$\left. \begin{aligned} y &= \rho^{-1/2} \pi^{1/2} \exp -[(x - U_0 t)^2 / 4\rho] \cos k_0(x - V_0 t) \\ &\quad = f_0(x - U_0 t) \cos k_0(x - V_0 t), \\ -\frac{\partial y}{\partial x} &= k_0 \ddot{y} + \frac{x - U_0 t}{2\rho^{3/2}} \exp -[(x - U_0 t)^2 / 4\rho] \cos k_0(x - V_0 t) \\ &\quad = f_1(x - U_0 t) \cos [k_0(x - V_0 t) + \arctan \theta], \\ \arctan \theta &= +\pi - \arctan (2k_0\rho/(x - U_0 t)). \end{aligned} \right\} \quad (3.013)$$

Consider the density of any one of the energy components, i.e.,  $a_i \left( \frac{\partial^i y}{\partial x^i} \right)^2$ , and assume an observer moving with velocity  $U_0$ , then  $(f(x - U_0 t))^2$  remains constant, while the varying  $\cos^2 [k_0(x - V_0 t) + \arctan \theta]$ , has, of course, the average value .5. Thus the mean energy density of each component remains constant in the observer's neighbourhood, and may, therefore, be considered as propagated at the velocity  $U_0$  under the limitations imposed by eq. (3.012). The general positive definite quadratic form for the energy, i.e.,  $\sum^N a_{ij} \frac{\partial y^i}{\partial x^j} \frac{\partial y^j}{\partial x^i}$  yields the same result, assuming a conservative system which amounts to saying

$$i+j = 2n \leq 2N.$$

The success of the method used for the proof is connected with the appearance of simple powers alone of  $k$  under the integration sign for successive derivatives of  $y$ , and the difficulties of treating the general phase function arise from the loss of this relation. Proper perspective is attained by using the integral

$$\int_{-\infty}^{\infty} e^{-\rho(k-k_0)^2 + jF(k; x, t)} dk. \quad \dots \quad (3.02)$$

Neglecting terms in  $k$  higher than the second, this integral is seen to be of the form (for  $\rho \gg F_{k_0 k_0}(t, x; k_0)$ ),

$$\begin{aligned} &\sim R.P. e^{jF(k_0; x, t)} \int_{-\infty}^{\infty} e^{-(\rho + jF_{k_0 k_0})z^2 + jF_{k_0}(k_0; x, t)z} dz \\ &\quad = f_0(F_{k_0}(k_0; x, t)) \cos F(k_0; x, t). \end{aligned} \quad (3.021)$$

Evidently the amplitude factor  $f_0(F_{k_0})$  remains constant for  $x$  and  $t$  values governed by  $dF_k = 0$  (cf. eq. 2.061). This new point of view, then, again leads to eq. (2.081) for the generalized group velocity  $U_2$ , but complications arise in attempting to correlate this value with energy transfer. This is because

$$\frac{\partial y}{\partial x} = R.P. \int_{-\infty}^{\infty} \frac{\partial F(k; x, t)}{\partial x} e^{-\rho(k-k_0)^2 + jF(k; x, t)} dk \\ (\sim f_1(k_0, x, t) \cos F(k_0; x, t)), \quad (3.022)$$

and  $\frac{\partial F}{\partial x}$  cannot be expected in general to be of the form

$f\left(\frac{\partial F}{\partial k}\right)$ . Special supplementary conditions are required

to assure that  $f_1(x, t; k_0)$  is, except for slowly varying functions of  $x$  and  $t$ , essentially of the type  $f_1(F_{k_0})$ .

Similar considerations affect  $\frac{\partial^n y}{\partial x^n}$ . If now the integrals for  $\frac{\partial^n y}{\partial x^n}$  are substituted in the general energy expression

$$\sum_i \sum_j a_{ij}(x) \frac{\partial^i y}{\partial x^i} \frac{\partial^j y}{\partial x^j}$$

( $i+j=2n+1$  gives the dissipation terms), it may be inferred that only those mean energy densities for which  $(f_i f_j \alpha_{ij})$  are essentially governed by  $F_{k_0}$  will move with the velocity  $U_2$ . It seems of particular interest that using a different method of approach we are able to exhibit a whole category of media for which energy is propagated with the group velocity  $U_2$  (cf. section V.).

First, however, a theorem suggested by Tonks \* will be examined †. This theorem, based on empirical study of five cases of wave motion, states that the group velocity is the ratio of the product of the phase velocity and the doubled interactive energy density to the total energy density. With the notation  $\epsilon_i$  for interactive energy the theorem is expressed

$$U\epsilon = 2V\epsilon_i. . . . . \quad (4.00)$$

Tonks's examples were all chosen so that only the first

\* Tonks, Phys. Rev. xxxiii. p. 239 (1929).

† D. G. Bourgin, Phys. Rev. xxxiii. p. 1072 (1929).

derivative of  $y$  occurred in the potential energy. If the equation for the vibrating rod

$$\frac{\partial^2 y}{\partial t^2} = \frac{\partial^4 y}{\partial x^4}. \quad \dots \quad (4.01)$$

be considered, it appears that the potential energy is entirely interactive, but since the vibrations are transverse the kinetic energy is not. Tonks's theorem would require  $U=V$  instead of the correct  $U=2V$ . That the theorem cannot be true in general is already evident from the fact that according to it one derives the clearly fallacious result that an upper limit for  $U/V$  is determined, namely 2. The Havelock theorem may be expressed

$$U = \frac{2V}{\epsilon} \sum_{\sigma} \sigma W_{\sigma}, \quad \dots \quad (4.02)$$

where  $W_{\sigma}$  is the mean potential energy associated with  $\left(\frac{\partial^{\sigma} y}{\partial x^{\sigma}}\right)^2$ . This is the corrected form of Tonks's theorem for this class of media and shows that, instead of an invariable factor 2, one must use a multiplier varying with the order of the derivative in the potential energy. That eq. (4.02) should be valid for media other than the generalized Havelock class of eq. (3.03) is not to be expected.

One conceives now a medium capable of supporting a sine or cosine wave non-linear in  $x$  and  $t$ . In the example chosen below, a non-negligible dissipation term enters, yet it will be demonstrated that, using the generalized group velocity  $U_2$ , one is entitled to speak of mean transmission of energy with group velocity. Consider then the class of equations

$$\rho \frac{\partial^2 y}{\partial t^2} = P \frac{\partial}{\partial x} \phi_x^{-2} \frac{\partial}{\partial x} y + P(\phi_{xx}/\phi_x^3) \frac{\partial y}{\partial x} - hy, \quad (5.00)$$

where

$$\phi_x = \frac{\partial \phi}{\partial x}, \text{ etc.,}$$

with  $\rho$ ,  $P$ , and  $h$  positive constants and  $\phi_{xx} (\neq 0)$  is of one sign in the range of discussion. A travelling wave solution is easily found to be

$$y = \cos k(\phi(x) - nt). \quad \dots \quad (5.01)$$

It is of interest to say a few words about eq. (5.00) independently of the announced purpose of the discussion of this section. One reason for the introduction of a defining equation of the type given is the opportunity furnished of distinguishing again between mathematical and physical equivalence. First it will be shown that

$$P\phi_{xx}/\phi_x^{-3} \frac{\partial y}{\partial x}$$

is a dissipative term \* or connected with an energy source depending on the sign of  $\phi_{xx}$ . One demonstration of the non-conservative character of eq. (5.00) depends on the fact that it is not the Euler equation of a calculus of variations problem, *i.e.*, there do not exist point functions T and W for which the Hamiltonian Variational integral gives eq. (5.00). The justification of this remark lies in the theorem (of the inverse problem in the calculus of variations) † to the effect that the necessary condition for a linear equation to be derived in such a way is that the equation be self-adjoint and eq. (5.00) is not.

\* Physical verification is also afforded by the reasoning about the work expression over the length  $dx$

$$W dx = dx P \int_{y_1}^{y_2} \phi_{xx} \phi_x^{-3} \frac{\partial y}{\partial x} dy. \quad \dots \dots \dots \quad (B)$$

This result is arrived at by looking upon eq. (5.00) as the equation of a vibrating string, for instance, and arguing that the force/unit initial length represented by the integrand term, acts in the direction of vibration, namely, along  $y$ . A little study shows that  $W$  depends on the path taken in the  $x, t$  plane. With the interpretation that the work at a fixed point  $x$  on the string is desired, the path to be chosen is evidently that range of values through which the string is carried during the time required for  $y$  to go from  $y_1$  to  $y_2$ . Accordingly, for greater ease in manipulation the space derivatives will be replaced by a time derivative. From the solution eq. (5.01), there follows

$$\frac{\partial}{\partial x} y = -\frac{k}{n} \phi_x \frac{\partial y}{\partial t},$$

and eq. (B) is equivalent to

$$dx P\phi_{xx}\phi_x^{-3} \int_{t(y_1)}^{t(y_2)} \frac{\partial y}{\partial x} \frac{\partial y}{\partial t} dt = -dx P \frac{k}{n} \phi_{xx} \phi_x^{-2} \int_{y_1}^{y_2} \frac{\partial y}{\partial t} dy.$$

Since  $y$  increasing carries with it  $\frac{\partial y}{\partial t} > 0$ , and  $y$  decreasing,  $\frac{\partial y}{\partial t} < 0$ , the integrand is always of one sign, and hence grows steadily in value with increasing time. This is another way of saying that energy is being imparted (extracted) to the system according to the inequalities

$$\phi_{xx} < 0, > 0.$$

† Hirsch, *Math. Ann.* (1897).

However, it is possible to find a multiplicative factor which will make eq. (5.00) self-adjoint, namely,

$$R = \phi_x.$$

Then

$$\rho\phi_x \frac{\partial^2 y}{\partial t^2} = \phi_x P \frac{\partial}{\partial x} \phi_x^{-2} \frac{\partial y}{\partial x} + P \phi_{xx} \phi_x^{-2} \frac{\partial y}{\partial x} - \phi_x h y \quad (5.001)$$

is self-adjoint and thus represents a conservative system. The equation has the same solutions as before, but though the results are mathematically equivalent the physical system is altogether different \*, since there is now no dissipation (either positive or negative). The kinetic energy density, for instance, is  $\frac{1}{2}\rho\phi_x \left(\frac{\partial y}{\partial t}\right)^2$ , whereas for eq. (5.00) it is  $\frac{1}{2}\rho \left(\frac{\partial y}{\partial t}\right)^2$ . The potential energy density for eq. (5.001) is

$$\frac{1}{2} \left( P \phi_x^{-1} \left( \frac{\partial y}{\partial x} \right)^2 + h y^2 \phi_x(x) \right).$$

The same type of disturbance is propagated in the first case because of energy rapport with external sources or sinks, in the second because of variations (with  $x$ ) of the elastic and inertial coefficients.

In generalizing, now, the method of Ferrari † to apply to dissipative media, one writes the key equation for energy changes in the length  $x_1 \rightarrow x_2$  as

$$dE = -d\omega + dF, \dots \quad (5.02)$$

where  $dE$  is the energy increment and  $d\omega$  and  $dF$  are the work done by the system and added to the system respectively. Hence

$$\frac{\partial}{\partial t} \int_{x_1}^{x_2} e dx = - \frac{\partial}{\partial t} \int_{x_1}^{x_2} \frac{\partial \omega}{\partial x} dx + \int_{x_1}^{x_2} \frac{\partial f}{\partial t} dx; \quad f = \frac{\partial F}{\partial x}, \quad e = \frac{\partial E}{\partial x}, \quad \dots \quad (5.021)$$

where  $e$  and  $f$  are dimensionally densities. The amended equation of continuity is

$$\frac{\partial e}{\partial t} + \frac{\partial}{\partial x} U e - \frac{\partial f}{\partial t} = 0, \quad \dots \quad (5.022)$$

\* The physical non-equivalence is obvious in the event of an applied force  $F(x, t)$  for eq. (5.00) would become  $L(y) = F(x, t)$ , which is different from  $\phi_x L(y) = F(x, t)$ , which results from eq. (5.001).

† O. Ferrari, *Rendiconti R. Acad. Lincei*, xxii. p. 761 (1913).

where the arbitrary function, which may be added without affecting the integral relationship eq. (5.021), is taken to be 0. One may therefore define the mean energy flow by

$$\bar{U} = \overline{\frac{\partial \omega}{\partial t}} / \bar{e}, \quad \dots \dots \dots \quad (5.03)$$

where the bars denote a time average. The purpose of the ensuing analysis is to show that

$$U = U_2.$$

The rate at which energy is contributed to the system is \*

$$\begin{aligned} \frac{\partial F}{\partial t} &= + \frac{\partial}{\partial t} \int_{x_1}^{x_2} \int_{y_1}^y P \phi_{xx} \phi_x^{-3} \frac{\partial y}{\partial x} dy dx \\ &= + \frac{\partial}{\partial t} \left( \int_{x_1}^{x_2} \int_{t(y_1)}^t P \phi_{xx} \phi_x^{-3} \frac{\partial y}{\partial x} \frac{\partial y}{\partial t} dt dx \right) \\ &= + \int_{x_1}^{x_2} P \frac{\phi_{xx}}{\phi_x^3} \frac{\partial y}{\partial x} \frac{\partial y}{\partial t} dx. \quad \dots \quad (5.04) \end{aligned}$$

Hence

$$\frac{\partial}{\partial t} (E - F) = \frac{\partial}{\partial t} \int_{x_1}^{x_2} e dx - \int_{x_1}^{x_2} P \phi_{xx} \phi_x^{-3} \frac{\partial y}{\partial t} \frac{\partial y}{\partial x} dx. \quad (5.041)$$

Plainly

$$e = \frac{1}{2} \left[ \rho \left( \frac{\partial y}{\partial t} \right)^2 + P \phi_x^{-2} \left( \frac{\partial y}{\partial x} \right)^2 + hy^2 \right]. \quad \dots \quad (5.05)$$

Therefore eq. (5.041) becomes

$$\int_{x_1}^{x_2} \rho \frac{\partial y}{\partial t} \frac{\partial^2 y}{\partial t^2} + P \phi_x^{-2} \frac{\partial y}{\partial x} \frac{\partial^2 y}{\partial t \partial x} + hy \frac{\partial y}{\partial t} - P \phi_{xx} \phi_x^{-3} \frac{\partial y}{\partial t} \frac{\partial y}{\partial x} dx. \quad \dots \quad (5.042)$$

Substituting for  $\frac{\partial^2 y}{\partial t^2}$  from eq. (5.00) gives for the right member of eq. (5.001),

$$\int_{x_1}^{x_2} \frac{\partial}{\partial x} P \phi_x^{-2} \frac{\partial y}{\partial x} \frac{\partial y}{\partial t} dx = - \frac{d\omega}{dt}. \quad \dots \quad (5.043)$$

\* Assuming for the moment that  $\phi_{xx} > 0$ , the correctness of the sign assignment is at once supported by the fact that  $\frac{\partial y}{\partial x} \frac{\partial y}{\partial t}$  is intrinsically negative.

The rate of doing work at a boundary is therefore manifestly

$$P\phi_x^{-2} \frac{\partial y}{\partial t} \frac{\partial y}{\partial x}$$

and

$$U = \frac{2P\phi_x^{-2} \frac{\partial y}{\partial x} \frac{\partial y}{\partial t}}{\rho \left( \frac{\partial y}{\partial t} \right)^2 + P\phi_x^{-2} \left( \frac{\partial y}{\partial x} \right)^2 + hy^2}, \quad \dots \quad (5.06)$$

where the averages are taken with respect to time. On using eq. (5.01) there results

$$U = \frac{2P\phi_x^{-1}kn}{\rho n^2 + Pk^2 + h}. \quad \dots \quad (5.061)$$

From eq. (5.00)

$$\begin{aligned} \rho n^2 &= Pk^2 + h, \\ U &= Pk/\rho n\phi_x \end{aligned} \quad \dots \quad (5.062)$$

But from eq. (2.081)

$$\begin{aligned} U_2 &= \phi_x^{-1} \frac{dn}{dk} = Pk/\rho n\phi \\ &= U \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (5.07) \end{aligned}$$

It is not difficult to establish that starting with eq. (5.001) with the new energies that eq. (2.07) again gives the group velocity as the propagation rate of the energy\*.

#### APPENDIX.

Related to the subject-matter of this paper is the question of representing a finite group, roughly speaking, a function which is sensibly zero except for a limited range of values of the argument, by an exponential series rather than an integral. Restricting attention to simple harmonic waves one may bar out immediately the Fourier

\* If the transformation  $z = \phi(x)$  be used, eq. (5.00) becomes the conventional constant coefficient damped wave equation of a new medium. One may look on the  $x$ -axis as being an arbitrary direction of projection of the motion—the physical problem is different, but the results regarding group velocity are identical with those derived in this paper.

series in integral multiples of the argument or the cases where the argument varies by factors of the form  $\sum_1^n n_i \alpha_i$ ,

where the  $\alpha_i$  are fixed and the  $n_i$  are integers; for, in both cases, one has periodic or quasi-periodic properties of the functions so represented. The question merits consideration because of the various recent attempts in the physical literature to utilize exponential series in this way. For instance, Flamm \*, in his work on packets and the quantum theory, represents a limited group for  $H_2$  by a series of the form

$$\psi(x, t) = \sum a_i e^{j(\lambda_i x + \nu_i t)}. \quad \dots \quad (6.00)$$

The conditions of Flamm's problem assure the absence of a finite limit point for the  $\lambda$ 's. Considering  $t$  fixed for the moment, the character of the series and the function associated bear discussion only after imposing some sort of convergence condition. If the series in  $x$  be uniformly convergent over the infinite interval, then the function represented is an almost periodic function in the sense of Bohr †—in other words, any range of values almost recurs an infinite number of times in conflict with Flamm's assumption. If the convergence restriction be lightened, it seems to be natural for the quantum theoretical interpretation that it be the Fourier representation ‡, in the broad sense, of the function associated, i. e., if

$$f(x) \sim \sum a_i e^{j\lambda_i x}, \quad \dots \quad (6.01)$$

$$a_i = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T}^T f(t) e^{-j\lambda_i t} dt. \quad \dots \quad (6.02)$$

However, in the first case, or the more general situation

\* Flamm, *Phys. Zeit.* xxiv. p. 427 (1928).

† H. Bohr, *Acta Math.* i. 111 for 1924–1926. It is assumed that the  $\lambda_i$  are real and have no finite limit point.

‡ The term "represent" describes the satisfaction of an inner relationship—here the truth of the Parseval equation.

$$\sum |a_i|^2 = L \frac{1}{T} \int_{-T}^T |f(x)|^2 dx.$$

Hence  $f(x)$  and  $\sum a_i e^{j\lambda_i x}$  may not coincide over a set of points of finite measure.

for which eq. (6.02) still applies, the quantum theoretical condition

$$\int_{-\infty}^1 f\bar{f} dx = 1$$

cannot be satisfied, since clearly the integral is infinite.

As regards the general question of availability of a series of type eq. (6.01), in order to maintain eq. (6.02) one must permit a generalized almost periodicity if even so weak a restriction as  $\sum a_i^2 < M$  be imposed, and, of course, the non-vanishing mean square value over the infinite range means the group cannot be finite. Since the series determines the function up to an arbitrary function of mean square 0, over a finite range the function represented may differ from the sum function of the series, and, as a consequence, the energy densities may differ, too, which affects the physical importance of this salient. One may avoid the almost periodicity property even in the extended form and expand a fairly general function in a series such as eq. (6.01), which converges to it \* ; but then eq. (6.02) is unavailable and hence no energy interpretations are possible. This last procedure is the only one permitted for the finite group, since its mean square value is zero. Accordingly, even waiving the difficulties encountered when the variability of  $t$  is taken into consideration †, it appears that the exponential series, instead of the integral representation of a finite group, is physically deficient of much interest ‡.

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\* Besicovich, Proc. Lond. Math. Soc. xxv. p. 495 (1926), has shown that a  $f(x)$  bounded on  $-\infty < x < \infty$  has associated an infinitude of different series of exponential type which converge to it. On following out the proof it appears that these series must be of the class characterized as follows : there are a denumerable infinitude of base exponents, each of which is associated with an infinite number of integral multiples.

† With general multipliers for the  $t$ -term of the exponent, the problem is one in almost periodic functions of two variables.

‡ All this assumes that for the group application to be made the problem cannot be physically approximated by a fixed enclosed system. It is, of course, common knowledge that for *finitely* contained systems the functions connected with the associated boundary value problem are very often expansible in series of orthogonal or bi-orthogonal sets of functions determined by the "discrete" spectrum.

**LXXXVI. A new Polarization Effect in Discharge-Tubes.**

*By JOHN THOMSON, M.A., D.Sc., Natural Philosophy Department, the University, Glasgow \*.*

**1. Introduction.**

IT is the purpose of this paper to describe an interesting phenomenon connected with the exact measurement of "sparking potentials" in discharge-tubes at low gas pressures. The experiments were made in glass tubes containing hydrogen, the electrodes being parallel circular plates of copper. The effect observed is new, so far as the writer is aware. It suggests that the electrode surfaces play a most important part in determining the sparking potential at low gas pressures.

**II. Apparatus**

In all researches concerned with discharge-tubes it is of the utmost importance to record the exact nature of the tubes, gases, and electric circuits employed, for the significance of each factor can only be assessed when details are given, and apparently minor variations in experimental conditions have before now produced very considerable changes in results. It has therefore been thought advisable to describe fully the apparatus employed. The present experiments were incidental to a much more elaborate investigation of sparking potentials, using alternating currents at very high frequencies. The nature of the discharge-tubes was determined by this latter problem. Fortunately the tubes were quite suitable for the work now to be described.

*The Discharge-Tube.*—Fig. 1 is a diagram drawn to scale of a section of a typical discharge-tube. This was made in two exactly similar parts, the glass caps having been made to a design in a special mould. The circular electrodes, A, B, were of copper, their sections being very slightly convex and their edges carefully rounded. The copper tubes, C, D, were screwed to the electrodes and pierced with several holes, H<sub>1</sub>, H<sub>2</sub>, . . . H<sub>6</sub>. One of the tubes acted as an inlet and the other as an outlet for the

\* Communicated by the Author.

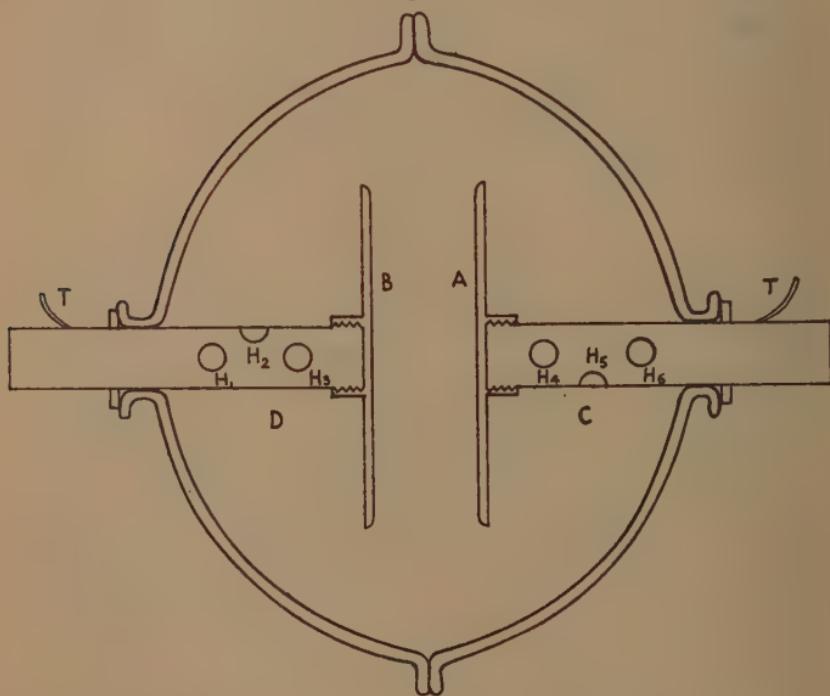
gas. To their ends were soldered tags, T, by means of which electrical connexions could be made. The joints of the tube and electrodes were sealed with a good hard wax of low vapour pressure. The absolute measurements were as follows :—

Diameter of each electrode = 8 cm.

Effective distance between the electrodes = 2.58 cm.

Greatest internal diameter of the glass envelope = 14 cm.

Fig. 1.



These dimensions ensured that the effect of wall-charges would be small.

*The Gas.*—The hydrogen used was prepared by the electrolysis of barium hydroxide, using a device which excluded oxygen from the hydrogen arm. The gas was dried by means of tubes of calcium chloride and phosphorus pentoxide. Finally, it was purified by means of liquid air. The best test of the purity of hydrogen is the nature of the curve obtained by measuring sparking potentials against gas pressure, using high-frequency

alternating potentials. This test indicated that in the present experiments the gas was exceptionally free from important contaminations, *i.e.*, from water-vapour and electro-negative gases.

*The Measurement of the Gas Pressure.*—The gas pressure was measured by the method described in a previous paper<sup>(1)</sup>. The discharge-tube system, consisting of three tubes similar to that shown in fig. 1 and a large reservoir, was filled to the highest pressure at which measurements were to be taken. This pressure ( $p_0$ ) was then read off directly by means of a U-tube manometer, containing Apiezon oil B. The lower pressures were obtained by exhausting the three discharge-tubes completely (using oil diffusion pumps), but maintaining the gas in the reservoir at the original pressure by means of a stop-cock. Then, when the gas is later shared between the reservoir and the tubes, the pressure is  $p_1 = kp_0$ , where  $k$  is a constant, depending only upon the relative volumes of the tubes and reservoir. After  $n$  evacuations of the tubes the pressure in the system is  $p_n$ , where  $p_n = k^n p_0$ . In the present experiments  $k$  had the value 0.766.

It is worthy of notice that this method of varying the pressure in a discharge-tube eliminates many of the difficulties which are usually encountered. By exhausting the discharge-tube after each set of readings has been taken the gas is renewed, and any impurity produced by the discharge is eliminated. On the other hand, by utilizing only the gas originally contained in the tubes and reservoir the quality of the original sample is maintained unchanged throughout all the readings, provided, of course, that the walls of the reservoir are free from contamination. In the present experiments the vacuum system had been in use with hydrogen as the filling gas for several months before any accurate measurements were taken.

*Measurement of the Sparking Potential.*—There are two distinct methods of measuring the potential difference required to initiate a discharge. The circuits used in the two cases are shown in figs. 2a and 2b.

In both circuits the (variable) output from the 3000-volt D.C. generator was connected across the potentiometer resistance  $R_2$ , of total value 12,000 ohms. The

sliding contact S, operated by a worm gear to enable fine adjustments to be made, tapped off part of the output, which was then smoothed by the circuit CIC. The condensers C were of the order of 1 microfarad, and the choke I was about 5 henries. The smoothed current then passed through the standard subdivided 2 megohms resistance  $R_0$ , and across part of the latter the electrostatic voltmeter V was connected. This instrument was

Fig. 2 a.

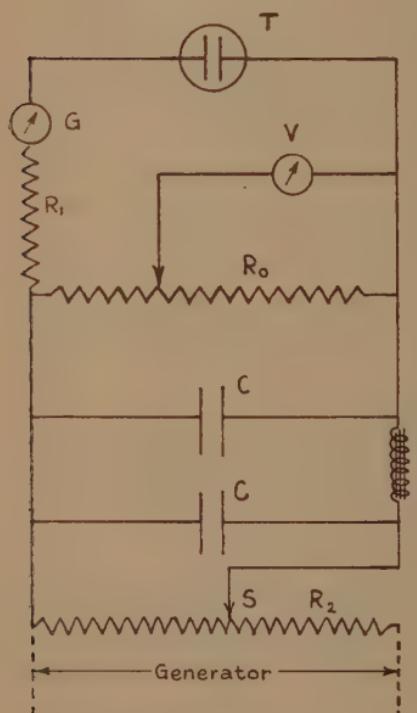
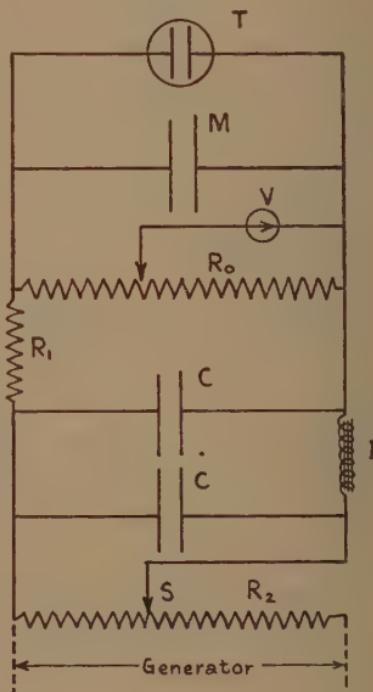


Fig. 2 b.



of Grade A accuracy, and gave its full scale deflexion for 600 volts. By means of the resistance  $R_0$  its sensitivity could be reduced to one-third. In each circuit  $R_1$  was a safety resistance of 2 megohms. In the circuit of fig. 2 a the galvanometer G in series with the discharge-tube T gave full scale deflexion for a few microamperes. In the circuit of fig. 2 b the condenser M in parallel with the tube was about 100 micro-microfarads.

Either circuit can be used to measure the striking potential of the discharge in T, for, so long as no current

is flowing through the tube, the voltmeter V measures the potential difference between the electrodes. In the circuit of fig. 2a the presence of a discharge is denoted by a current in the galvanometer, while in the other circuit, when a "flash" occurs, the reading of the voltmeter V falls suddenly.

### III. *The Experiments.*

First the circuit of fig. 2a was employed to measure the sparking potentials of the tube at different gas pressures. The results are shown in fig. 3, curve A. In this experiment there was some dubiety about the striking of the discharge. Owing to the high value of  $R_1$ , the stable form of the discharge, when it formed, was a corona. Hence the exact reading of the voltmeter V depended upon the sensitivity of G. Also, as was to be expected, certain "polarization" effects were observed. The first sparking potential at any given pressure was slightly less than the succeeding values.

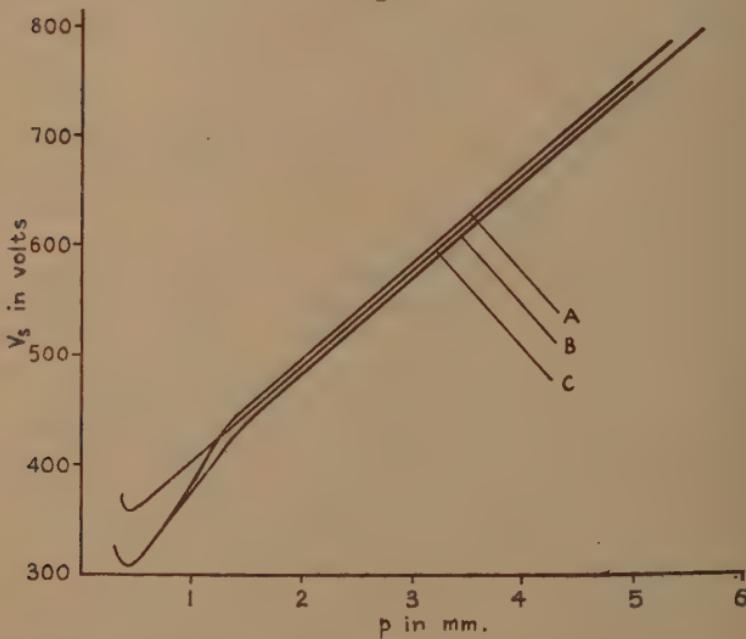
Using the circuit of fig. 2b, with which the results shown in fig. 3, curve B, were taken, this dubiety disappears. The capacity discharge or "flash" produces a definite sudden variation in the voltmeter reading, which could therefore be taken with the greatest accuracy of which the instrument was capable. Polarization effects with this circuit were also noticeably less. In general, however, the difference between the results obtained from the two circuits is not sufficiently pronounced to warrant the statement that one of them is unreliable.

*A New Effect.*—It will be observed that while the curves A and B of fig. 3 are straight lines (within the limits of experimental error) at the higher gas pressures, they become definitely convex upwards at pressures less than twice the critical value. This convexity is not found in certain curves obtained by previous investigators<sup>(5)</sup>, while in the results of others the curve connecting the sparking potential ( $V_s$ ) with the pressure ( $p$ ) is convex upwards over its whole length. In some previous measurements made by the present writer<sup>(1)</sup> the curves did not exhibit any trace of convexity upwards, and this suggested the following experiments.

An alternating potential difference at a frequency of about 6 megacycles per second was applied between the

electrodes of the discharge-tube, and was increased until a strong high-frequency glow occurred. The tube was then disconnected from the oscillatory circuit, and its sparking potential was measured by means of the circuit of fig. 2b. Then the gas pressure was reduced in the usual manner, another strong high-frequency discharge was passed, and the sparking potential was again measured. This procedure was repeated at each new gas pressure, until the latter was too low to allow a high-frequency discharge at 6 megacycles to be struck. (The minimum

Fig. 3.



sparking potential, when the electrodes are 2.58 cm. apart and the frequency is that mentioned above, occurs at 0.95 mm. of mercury.) The results are shown in fig. 3, curve C.

This last experiment was repeated, using an oscillator the frequency of which was about 60 megacycles per second. In this case high-frequency discharges could be struck at pressures lower than the critical pressure for the initiation of the steady discharge. Apart from minor variations of the order of the experimental error, a curve identical with C of fig. 3 was obtained at the gas pressures previously investigated. At the lower gas pressures the

continuation of curve C was found. At these low pressures it was observed that the current flowing in the high-frequency discharge had to be greater than a certain minimum for the full increase in  $V_s$  to be experienced.

#### IV. Discussion.

The writer has already pointed out <sup>(1)</sup> that when  $V_s$  is measured against  $p$ , using a high-frequency alternating potential and hydrogen as the filling gas, the curve is a straight line for high gas pressures, and is *never* convex upwards at any pressure (within the range investigated) if the gas is pure. The linearity of the  $V_s$ ,  $p$  relationship is indeed striking, and since the high-frequency striking potential can be measured (relatively) with the greatest accuracy, there can be no dubiety about the result. In the writer's earlier measurements of the striking potential, using a steady voltage, it happened that a high-frequency discharge was passed in the tube between all the readings. For this reason and in view of the effect just described the convexity upwards exhibited by curves A and B of fig. 3 was missed.

It must now be asked "What is the cause of the increase in the sparking potential produced by the passage of a high frequency discharge?" Three possible causes suggest themselves :

1. "Clean-up" of the gas in the tube during the high-frequency glow alters the nature of the filling gas.
2. The alternating discharge either builds up or breaks down electric charges on the walls of the tube.
3. The discharge produces changes in the electrode surfaces.

The writer cannot accept the first suggestion. The purification of the gas appeared to be quite adequate. No other changes occurred in the tube which might be ascribed to the same cause. Also, the tube could be made to return to its normal (lower) sparking potential by passing a direct-current glow for a few minutes. Finally, both the steady and the high-frequency alternating sparking potentials could be maintained constant at any particular pressure to within 5 volts in the first case and 1 volt in the second over months of working.

Neither can the second suggested cause be accepted. In the tube used wall effects should be small, although,

considering the extreme dryness of the gas used, it would be unsafe to say that they were negligible. But test experiments carried out in tube B of the previous investigation<sup>(1)</sup> and in another tube similar to that of fig. 1, but with the electrodes 4·9 cm. apart, showed changes in the sparking potential of the same type. The fact that  $V_s$ , in all three cases rose *just* to such a value that the convexity of the curve disappeared is strong evidence against the wall-effect suggestion.

An additional experiment performed with an Osglim lamp (the resistance in the base having been removed) is interesting. The sparking potentials measured on a standard electrostatic voltmeter of range 60–240 volts were as follows :—

A. With the “ beehive ” electrode as the anode

- (1)  $V_s$ , after passing a direct current discharge = 191 volts.
- (2)  $V_s$ , after passing a high-frequency discharge = 185 volts.

B. With the “ beehive ” electrode as the cathode

- (1)  $V_s$ , after passing a direct current discharge = 183 volts.
- (2)  $V_s$ , after passing a high-frequency discharge = 179 volts.

The electrodes in this discharge-tube are very far from the walls, and the purity of the neon gas is high. Yet the change in the sparking potential is quite marked.

The third suggestion—that the variation in  $V$  is due to a change in or on the surfaces of the electrodes—appears to the writer to be more likely. J. Taylor has discussed many such polarization effects in discharge-tubes, and has shown that it is possible by running a discharge to modify profoundly the electrodic surface layers, even in tubes which have been scrupulously treated to eliminate impurities on the walls or electrodes and in the gas<sup>(2)</sup>.

Let it be supposed that the high pressure part of a particular  $V_s, p$  curve can be represented by the equation

$$V_s = A + Bp \quad \dots \quad (1)$$

Then, as will be observed is the case in fig. 3 (curves A and B), it is possible to find another set of readings with another sample of gas at a later time which will obey the equation

$$V_s = A' + Bp \quad \dots \quad (2)$$

and A—A' is of the order of 15 volts. The writer has found this occurring many times in the course of his experiments. Indeed, in certain observations on the high-frequency discharge it has been found that there is a discontinuity in the  $V_s$ ,  $p$  curve, the two parts of which can be represented by equations of the form of (1) and (2). In this case, however, A'—A is seldom more than 5 volts and A is of the order of 100 volts. It appears likely, therefore, that the sparking potential of a discharge-tube at any given pressure is made up of two parts. One of these, since it does not vary with the gas pressure, might be assumed to be associated with the electrodes. This part is about 300 volts, using copper electrodes and hydrogen gas at low pressures and employing steady potentials to produce the discharge. The other part of the sparking potential, which varies directly with the number of molecules of gas between the electrodes, may be assumed to be due to the gas itself. Rewriting equation (1) in the appropriate form,  $V_s$  is given by

$$V_s = A + Bpd, \dots \quad (3)$$

where  $d$  is the distance between the electrodes, which are assumed to be arranged so that the electrostatic field due to their charges is substantially uniform. Then the constant B for the gas hydrogen, as determined by the present experiments, is 33.3 volts per cm. per mm. of mercury. The value obtained from the earlier experiments <sup>(1)</sup> was 38.8 expressed in the same units, while from the experiments of Townsend and Hurst <sup>(3)</sup> a value of about 36 may be deduced. The value of  $pd$  for which  $V_s$  is a minimum is given by the present experiments as 1.11 cm. by mm. of mercury. Townsend and Hurst give 1.15 for the same constant. It is the writer's opinion that the high value for B found in his earlier experiments was due to the relative impurity of the gas. He has already shown that the electrical properties of hydrogen depend to a very large extent on the dryness of the gas <sup>(4)</sup>.

Let it be assumed that, during the course of an experiment such as those described above, the electrode surfaces (or the gas layers on these surfaces) remain unchanged. Then the writer suggests that the value of A in equation (3) will also remain unchanged, and the  $V_s$ ,  $p$  curve will have no convexity upwards. It will (at all pressures greater than twice the critical pressure) be a straight line.

If, however, the discharges which occur during the course of the experiment produce changes in the electrode surfaces (or in the surface layers), then A will vary. It may either increase or decrease, but in general it will decrease as the gas pressure is reduced. In support of the contention that A is a function of the electrodes and not of the gas, it is worthy of notice that when the  $V_s$ ,  $p$  curve is non-linear, Paschen's law ceases to be obeyed exactly. This is an experimental result. There is no reason, *a priori*, why such non-linearity should imply the break-down of Paschen's law.

#### *Summary.*

1. It is shown that the sparking potential of a discharge-tube depends upon the nature of the discharge which has been passed through it previously, and that the passage of a high-frequency discharge may produce systematic variations in the "normal" sparking potential.

2. By passing a high-frequency discharge before reading the static sparking potential (the sparking potential when a steady potential difference is applied across the tube, and is very slowly increased), it is possible to make the mode of variation of the latter with the gas pressure obey the equation  $V_s = A + Bp$  at pressures greater than twice the critical value. In view of the fact that the sparking potential, using high-frequency alternating potentials, obeys a similar law, it is suggested that this equation represents the state of affairs when the surfaces of the electrodes remain the same throughout the experiment, and that, therefore, the value of the number A depends upon the electrodes, while the value of B depends only upon the gas.

It is a pleasure to express my gratitude to Professor E. Taylor Jones for the facilities to carry out these experiments and for his interest in the work. I wish also to thank the Executive Committee of the Carnegie Trust for a very useful Research Grant.

#### *References.*

- (1) *Phil. Mag.* xviii. p. 696 (1934).
- (2) *Ibid.* iii. p. 753 (1927).
- (3) *Ibid.* viii. p. 738 (1904).
- (4) *Ibid.* vii. p. 970 (1929).
- (5) Carr, *Phil. Trans. cci.* p. 403 (1903).

LXXXVII. *The Spontaneous and Artificial Transmutations of Atom Nuclei.* By Prof. K. C. KAR, D.Sc.<sup>†</sup>

**I**N the wave-statistical theory of spontaneous disintegration of  $\alpha$ -particles by radioactive atoms, recently developed by me <sup>‡</sup>, expressions for the disintegration constant and the radius of the core have been obtained simultaneously. The corresponding wave-mechanical theory, it may be noted, does not give the value of the radius of the core. This is among others one of the important advantages of the wave-statistical theory.

In the present paper we shall critically discuss the question of the radius of the core and shall show that the above wave-statistical theory may be extended to explain the emission of long-range  $\alpha$ -particles by radioactive substances. It will also be shown that the theory may be easily adapted to explain the well-known phenomenon of artificial disintegration, recently studied experimentally by Rutherford and his students.

Before we actually enter into the present discussion it will be advisable to give a brief summary of the previous paper. In doing so we shall incidentally discuss the validity of the approximations used before.

*Spontaneous Disintegration.*

It is supposed that within the nucleus there is a hard core where the whole of the charge is collected. Thus outside the core, but within the nucleus, the electric field varies inversely as the square of the distance. It is also assumed that, due to the very high value of the density inside the core, the phase space there acquires a little viscosity, on account of which there is a regular flow of  $\alpha$ -particles outward.

With these assumptions the R-solutions for inside and outside the core were respectively obtained as

$$R_1 = \text{const. } \frac{\sin \alpha_1 r}{r}, \quad \alpha_1^2 = \frac{8\pi^2 m E}{h^2} \left( 1 + \frac{b^2 h^2}{16\pi^2 E^2} \right), \quad (1)$$

<sup>†</sup>. Communicated by the Author.

<sup>‡</sup> K. C. Kar and A. Ganguli, Phil. Mag. xvi. p. 1907 (1933).

and

$$\left. \begin{aligned} R_2 &= \text{const. } \frac{\sqrt{\cot u}}{r} e^{\kappa(2u - \sin 2u)}, \quad \cos^2 u = \frac{\alpha_2 r}{4k}, \\ \alpha_2 &= \frac{4\pi\sqrt{2m(E + U_0)}}{\hbar}, \quad k = \frac{4\pi z^* e^2}{\hbar\sqrt{2(E + U_0)/m}}, \end{aligned} \right\} . \quad (2)$$

where  $E$  is the energy of the  $\alpha$ -particle,  $b$  the damping or the viscosity coefficient,  $U_0$  the surface potential of the hard core, and  $z^*$  the effective atm. no. The other symbols not explained have their usual meaning.

At the surface of the hard core the following boundary conditions should evidently be satisfied :

$$\left. \begin{aligned} R_1 &= R_2, \\ \frac{dR_1}{dr} &= \frac{dR_2}{dr}, \end{aligned} \right|_{r=r_0}$$

or

$$d \log R_1 = d \log R_2. \quad \dots \quad (3)$$

From (1) and (2), and the boundary conditions (3), we deduced in the previous paper two important relations, viz., (33 a, b). The approximations used for that at first sight appear to be wrong, because the approximate value of  $\alpha_2$  is used from the beginning. So we shall here use the correct values of  $\alpha_1$ ,  $\alpha_2$ . But we arrive at the same result as before.

The left-hand side of (3) gives

$$\begin{aligned} \alpha_1 \cot \alpha_1 r_0 - \frac{1}{r_0} &= \alpha_1 \cdot \frac{1 - \frac{(\alpha_1 r_0)^2}{2}}{\alpha_1 r_0 - \frac{1}{6}(\alpha_1 r_0)^3} - \frac{1}{r_0} \\ &= \frac{1}{r_0} \left\{ 1 - \frac{1}{3} (\alpha_1 r_0)^2 \right\} - \frac{1}{r_0}, \end{aligned}$$

neglecting higher terms,

$$= -\frac{1}{3} \alpha_1^2 r_0 = -\frac{r_0}{3} \cdot \frac{8\pi^2 m E}{h^2} \left( 1 + \frac{b^2 h^2}{16\pi^2 E^2} \right) . \quad (4)$$

Again, the right-hand side of (3) gives

$$-\frac{1}{r_0} + \frac{\alpha_2}{16k \sin^2 u_0 \cos^2 u_0} - \frac{\alpha_2}{2} \tan u_0 ;$$

on substituting for  $u_0$  from (2) and remembering that  $\alpha_2 r_0 \ll k$  we get

$$\begin{aligned} & -\frac{1}{r_0} + \frac{1}{4r_0} \left( 1 + \frac{\alpha_2 r_0}{4k} \right) - \frac{1}{r_0} \sqrt{\alpha_2 r_0 k} \left( 1 - \frac{\alpha_2 r_0}{8k} \right) \\ & = -\frac{3}{4r_0} + \frac{\alpha_2}{16k} - \frac{1}{r_0} \sqrt{\alpha_2 r_0 k} \left( 1 - \frac{\alpha_2 r_0}{8k} \right) \end{aligned}$$

and on substituting for  $\alpha_2$ ,  $k$ , and simplifying

$$= \frac{1}{r_0} \left\{ -\frac{3}{4} - \frac{4\pi}{h} \sqrt{mz^* e^2 r_0} \right\} + \frac{\alpha_2}{8k} \left\{ \frac{1}{2} + \frac{4\pi}{h} \sqrt{mz^* e^2 r_0} \right\}. \quad (5)$$

On comparing the magnitudes of the different quantities involved, it may be seen that the first term of (5) is very great compared with the second, and also with the expression (4). Thus on equating (4) with (5) we get

$$\frac{1}{r_0} \left\{ -\frac{3}{4} - \frac{4\pi}{h} \sqrt{mz^* e^2 r_0} \right\} = 0 \quad \dots \quad (6)$$

and

$$-\frac{r_0}{3} \cdot \frac{8\pi^2 m E}{h^2} \left( 1 + \frac{b^2 h^2}{16\pi^2 E^2} \right) = \frac{\alpha_2}{8k} \left\{ \frac{1}{2} + \frac{4\pi}{h} \sqrt{mz^* e^2 r_0} \right\}. \quad (7)$$

From (6) we get at once

$$r_0 = \left( \frac{3}{16\pi} \right)^2 \cdot \frac{h^2}{mz^* e^2} \quad \dots \quad (8)$$

being the value of the radius of the hard core obtained before (*cf.* (35)).

On substituting in (7) the value of  $(mz^* e^2 r_0)$  from (8), we get

$$\begin{aligned} & \frac{r_0}{3} \cdot \frac{8\pi^2 m E}{h^2} + \frac{r_0}{3} \frac{8\pi^2 m E}{h^2} \cdot \frac{b^2 h^2}{16\pi^2 E^2} = \frac{\alpha_2}{32k} \\ & = \frac{E}{16z^* e^2} + \frac{U_0}{16z^* e^2}, \quad \dots \quad (9) \end{aligned}$$

on substituting for  $\alpha_2$  and  $k$ . Now on equating the first terms on either side, which are of the same order and greater than the second terms, we get

$$r_0 = \frac{2}{3} \left( \frac{3}{16\pi} \right)^2 \cdot \frac{h^2}{mz^* e^2}, \quad \dots \quad (10)$$

giving the value of  $r_0$ . It is interesting to note that  $r_0$  thus obtained has the value which is just  $2/3$  of that already obtained in (8).

On equating the second terms of (9) we get

$$b^2 = \frac{3}{8mz^*e^2r_0} \cdot U_0 E.$$

On defining the linear damping coefficient as  $4\pi\lambda_1=b$ , we get

$$\lambda_1 = \frac{a}{h} \sqrt{U_0 E}, \dots \dots \quad (11)$$

where  $a=0.82$  if one substitutes for  $r_0$  from (8), and  $a=1$  if  $r_0$  is substituted from (10). It should be noted that the former value is slightly greater than the one obtained in my previous paper, viz.,  $a=0.61$ . However, the latter value is exactly the same as that given by the approximate method discussed in the previous paper. The slight differences in the numerical constant are apparently due to the approximations involved in the different cases. There is no use pushing the discussion any further at present, as the final formula for the disintegration constant involves an unknown averaging (normalizing) factor.

Now the disintegration constant and the damping coefficient are respectively defined as

$$\lambda = -\frac{1}{N_a} \frac{dN_a}{dt}, \quad \lambda_1 = -\frac{1}{N} \frac{dN}{dt}, \dots \quad (12)$$

where  $N_a$  is the number of particles in a thin shell just inside the hard core and  $N$  the total number within it.

Since

$$\frac{dN_a}{dt} = \frac{dN}{dt}$$

and

$$\left. \begin{aligned} \frac{N_a}{N} &= \text{const. } \frac{\sin^2 \alpha_1 r_0}{r_0^2} r_0^2 \Delta r_0 \\ &= \text{const. } \frac{\cot u_0}{r_0^2} \cdot e^{2k(2u_0 - \sin 2u_0)} r_0^2 \Delta r_0, \end{aligned} \right\}. \quad (13)$$

we have from (12 and (11)

$$\lambda = \frac{\frac{a}{h} \sqrt{U_0 E}}{\text{const. } \cot u_0 \Delta r_0} e^{-2k(2u_0 - \sin 2u_0)}.$$

On combining the constants, the above may be written in the simple form

$$\lambda = \text{const.} \frac{\sqrt{U_0 E}}{\cot u_0} e^{-2k(2u_0 - \sin 2u_0)} \dots \quad (14)$$

in agreement † with formula (44) of the previous paper.

### *Emission of Fast Particles.*

As a result of a series of experiments carried out recently, Rutherford ‡ and others have shown that from a number of radioactive elements groups of fast particles are often emitted. Moreover, the elements which were supposed to emit particles of given velocity really give out particles of velocities varying over a small range. Thus formula (14) must be modified.

From a numerical computation of the energy of the disintegrated  $\alpha$ -particles, it can be shown that they become free at least at a distance  $10^{-13} \rightarrow 10^{-12}$  cm. from the centre of the core. On the other hand, formula (8) gives for the radius of the hard core  $r_0 \sim 10^{-15}$  cm. for radioactive substances. So we have to suppose that the region between  $10^{-15}$  and  $10^{-13}$  cm. is filled with electrically neutral particles. Evidently it corresponds to the neutral shell of Rutherford. Since it is outside the charged core the electrical force of repulsion is Coulombian in this region.

According to Rutherford the shell is filled with polarized helium atoms. But it appears that a more general assumption would be to suppose that the shell is packed with large numbers of  $\alpha$ - and  $\beta$ -particles such that the net charge is zero. The particles may possibly circulate in a number of orbits under a polarization field. Thus the neutral shell may be supposed to consist of a number of thin shells of particles. Now as soon as an  $\alpha$ -particle comes out of the core and passes through the shell, it will naturally interact with the circulating  $\alpha$ -particles in the thin shells.

† The slight difference in  $r_0$ , due to algebraic mistake, has been corrected here. It may be noted that the mistake does not materially affect the theoretical values of the previous paper, since  $r_0$  is practically constant for the different elements in the group.

‡ Rutherford, Ward, and Lewis, Proc. Roy. Soc. cxxxii. p. 684 (1931); Rutherford, Wynn-Williams, and Lewis, Proc. Roy. Soc. cxxxiii. p. 351 (1931).

And as a result of the interaction an  $\alpha$ -particle which was originally present in the shell is ejected.

It is now evident that the rate of disintegration is really the rate of ejection from the thin shells. Formula (14) gives the rate at which the  $\alpha$ -particles enter the shell from the hard core within. Therefore the rate we require is the rate given in (14) multiplied by the number of  $\alpha$ -particles present in an excited state in the particular thin shell. Supposing the number of excited  $\alpha$ -particles to be proportional to the number of particles which are just free, *i.e.*, which are about to move in hyperbolic orbits, we have for the number †

$$N_1 = N \cdot \frac{A_1}{r^2} \sin^2 \frac{2\pi mv}{h} r_1 \cdot 4\pi r_1^2 dr_1, \dots \quad (15)$$

where  $N$  is the total number in the given shell of radius  $r_1$ ,  $v$  the velocity of the particle in the shell,  $m$  the mass of the particle, and  $A$  the averaging (normalizing) factor.

Thus the rate of ejection of the  $\alpha$ -particles from the shell is given by a formula of the form

$$\lambda = \text{const.} \frac{\sqrt{U_0 E}}{\cot u_0} e^{-2k(2u_0 - \sin 2u_0)} \cdot \sin^2 \frac{2\pi mvr_1}{h}, \quad (16)$$

where the factor  $dr_1$ , the thickness of the shell, is absorbed in the const., which is to be evaluated from numerical computation. It will be shown presently that for any

shell  $\sin \frac{2\pi mvr_1}{h} = 1$ , if it is supposed that the  $\alpha$ -particles

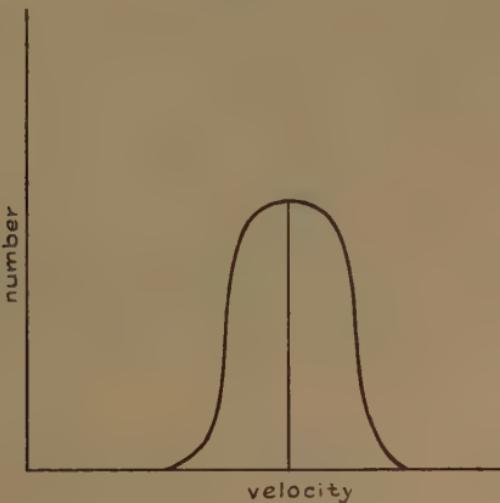
belonging to the group are all emitted with the mean velocity. In that case formula (16) evidently reduces to (14).

As already pointed out, Rutherford and others have shown that the radioactive elements emit  $\alpha$ -particles with velocities varying over a small range. Furthermore, the fast  $\alpha$ -particles emitted by RaC, ThC, etc., when carefully studied, are found to form a number of groups of different mean velocities. In all cases the variation

† For hyperbolic orbits the eigenfunction is  $A \cdot \frac{e^{ikr}}{r}$ , which is also the solution of the wave equation for large distances (see Sexl, *Zeits. f. Phys.* lvi, p. 62 (1929)).

of the number with the velocity is given by a curve of the form :—

Fig. 1.



It is evident that the above variation is well explained by the  $\sin^2$ -factor in (16), when  $r_1$  is given the mean value for the particular group or shell. Again, since the limiting velocities for which the number vanishes are known from the experiment, the corresponding limiting values of  $r_1$  are known from the condition that the  $\sin^2$ -factor is zero at these limits. One must, of course, remember that the angle  $\frac{2\pi mvr_1}{h}$  lies between  $\pi$  and  $2\pi$ ,

the zero value being excluded for obvious reason.

It should be noted that when we consider the variation of  $\lambda$  due to the  $\sin^2$ -factor we ignore its variation due to the exponential and the associated factors, which also depend on velocity. It is justified because the velocity varies over a small range for a given group. And for such small variations the above factors are practically constant. We should, however, take the average velocity in the exponential and other factors. Here the question arises whether the average value should be that corresponding to the group in question or the main group for the particular element. In the former case we have to tacitly assume that there must be as many groups of  $\alpha$ -particles in the hard core as they are actually observed

experimentally. This appears to be unlikely. In the latter case we must, of course, assume that the main group can excite different groups of particles in the shell.

We shall conclude the section by calculating the average radius of emission for a number of groups. It is evident that when we put for  $v$  and  $r_1$  in (16) their average values,

then  $\sin \frac{2\pi mvr_1}{h} = 1$ . Or we have

$$\frac{2\pi mvr_1}{h} = \frac{3\pi}{2} . . . . . \quad (17)$$

Substituting the experimental average value of the velocity ( $v$ ), we get the average radii of emission ( $r_1$ ), which are given in column 3 of the following table. The relative numbers of particles counted are given in column 2 :—

Substance.	Relative number.	$r_1 \times 10^{13}$ (cm.).	Observer.
RaC . . . . .	10 <sup>6</sup>	3.84	Rutherford, Ward, Lewis.
	0.49	3.70	
	16.7	3.53	
	0.53	3.47	
	0.93	3.44	
	0.60	3.40	
	0.56	3.37	
	1.26	3.33	
	0.67	3.29	
ThC . . . . .	0.21	3.27	
	$5.4 \times 10^5$	4.31	Rutherford, Wynn-Williams, Lewis.
	10 <sup>6</sup>	3.59	
	33.6	3.44	
" . . . . .	189	3.23	
	19	4.33	Rutherford, Wynn-Williams, Lewis.
AcC . . . . .	100	4.19	
	0.32	3.379	

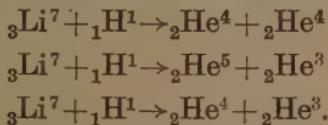
### Artificial Transmutation.

When the atoms of lighter elements are bombarded by  $\alpha$ -particles or protons, a certain small percentage of them is absorbed by the hard core of the atoms. As a result of that there is disruption of the atom-nucleus and consequent transmutation of elements. Now the absorption by the hard core followed by sudden increase of the density may be supposed to be due to the phase space

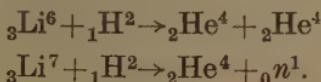
of the core acquiring temporarily the property of negative damping, *i.e.*, negative viscosity. The effect of the negative damping is evidently to produce a gradual increase of amplitude of the phase wave. It should be here noted that generally the damping coefficient for a fluid is positive. But there is no difficulty in imagining a negative damping coefficient or a negative viscosity when it is remembered that they are all relative. One can also easily imagine a mechanism by which a system may be made to possess negative damping.

Now, in the case of spontaneous disintegration the wave-equation (*cf.* (12) *l. c.*) for the hard core involves the square of the damping coefficient "b." So it is unaffected by the sign of *b* and may be used even in the present case. Thus the rate of absorption of the bombarding particles is given by the same formula (14) which gives the rate of spontaneous ejection of particles from the hard core.

As a result of the absorption the nucleus disrupts into a number of nuclei. Thus, for example, when lithium is bombarded by proton, the probable reactions are, according to Oliphant-Kinsey-Rutherford,<sup>†</sup>



Or when lithium is bombarded by heavy hydrogen particles, the reactions are



Taking the solution for the free nuclei in the same form as before, we have for the different transmutation products

$$\left. \begin{aligned} \lambda' &= C' \cdot \frac{\sqrt{U_0'E'}}{\cot u_0'} e^{-2k'(2u_0' - \sin 2u_0')} \sin^2 \frac{2\pi m'v'r_1'}{\hbar} \\ \lambda'' &= C'' \cdot \frac{\sqrt{U_0''E''}}{\cot u_0''} e^{-2k''(2u_0'' - \sin 2u_0'')} \sin^2 \frac{2\pi m''v''r_1''}{\hbar} \end{aligned} \right\} \quad (18)$$

and so on, where *v'*, *v''*, etc. are the velocities of the

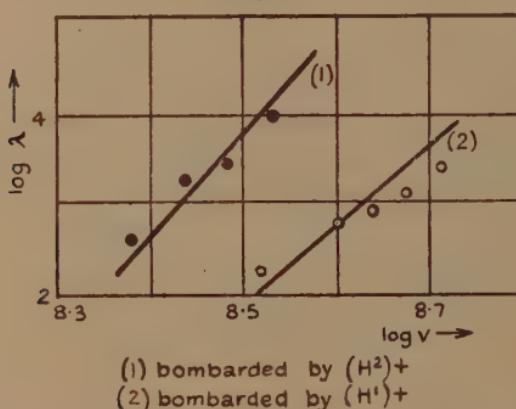
<sup>†</sup> Oliphant, Kinsey, and Rutherford, Proc. Roy. Soc. exli.p. 722 (1933).

particles formed,  $m'$ ,  $m''$ , etc., their masses and  $r_1'$ ,  $r_1''$ , etc., the radii of emission, i. e., the distances from the origin when they are just set free.

If we neglect the small variation of velocity within a given group of transmutation product and suppose all of them to be ejected with the mean velocity, the  $\sin^2$ -factor in (18) becomes unity. The formula now reduces to a simple form and can be used to find the variation of  $\lambda$  with the velocity of the bombarding particles. The theoretical curves giving such variations are indicated in fig. 2.

The curves show decidedly better agreement in the case of  $(H^2)^+$ . Now in (18)  $U_0$  denotes the surface energy

Fig. 2.



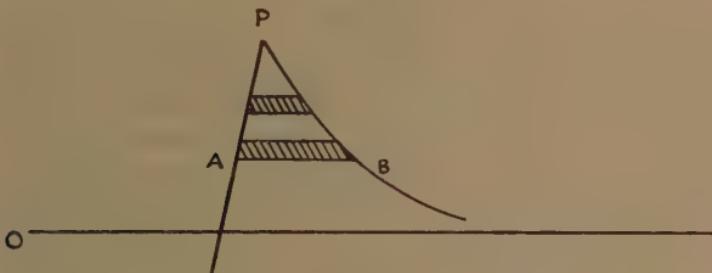
of the hard core and is of the nature of latent heat of evaporation from the surface of the core. So  $U_0$  may be taken to be proportional to the mass  $\dagger$  of the bombarding particle that is crossing the surface. Therefore the factor  $\sqrt{U_0 E} \sim m$ . And so the quantity of disintegration product should be less when the element is bombarded by lighter particles. It is encouraging to note that the above is qualitatively borne out by the experiment of Oliphant-Kinsey-Rutherford. The experimental value of the logarithmic difference of the quantities, when the bombardment is made by  $(H^2)^+$ - and  $(H^1)^+$ -particles, is 2; whereas the difference as given by the above factor is  $\log_{10} 2 = 0.3$ .

$\dagger$  If it is supposed that the protons constituting the bombarding particle are bound together, while crossing the surface, then probably  $U_0 \sim m^2$ .

*Potential Barrier.*

The wave-statistical theory developed is based on Rutherford's model of nucleus. However, nowadays, Gamow's picture of potential barrier seems to have replaced the above model. But it can be easily seen that there is a close agreement between the two. According to Gamow the potential within the nucleus varies as shown by the curve. At a distance greater than OP the potential is Coulombian, varying inversely as the distance. On the other hand, for distances less than OP the potential decreases with the distance. The  $\alpha$ -particles are packed within the sphere of radius OP, which is evidently Rutherford's hard core, where the whole of the nuclear charge is stored up. Beyond OP

Fig. 3.



there is the neutral shell of Rutherford. There are stationary orbits in the neutral shell. And any particle going out of the hard core is caught for a while in one of these resonance levels and *vice versa*. This explains the existence of holes in the potential wall (shaded in fig. 3).

It may not be out of place to make a few remarks as to how, according to Gamow and others, the particles cross the potential wall, *i.e.*, the surface of the hard core. Gamow assumes that the crossing is explained by Heisenberg's Principle of Uncertainty. But it appears to me to be fallacious to apply Heisenberg's principle to this case. The rate of disintegration, however small, has a definite value. It is a phenomenon known with a certainty. It is not therefore proper to take help of the uncertainty principle, which gives a measure of the "unknowable," to explain what is known definitely with definite experimental values. After Gamow's theory

Born †, Sexl ‡, and others deduced a similar formula on assuming a definite transmissibility of the barrier. Obviously there can be no objection, as in Gamow's theory, to such an assumption. However, in all these wave-mechanical theories it is assumed that the energy of the disintegrating  $\alpha$ -particles is partly real and partly imaginary. The assumption of particles having imaginary energy is certainly open to criticism. In a recent paper on the subject Sexl § has suggested that one has to make the above assumption because the waves within the nucleus are damped.

It may be noted that no difficulties as above, are met with in the wave-statistical theory, based on the hypothesis of a viscous phase space for the hard core.

### *Radius of the Core.*

Formula (8) gives the distance of the core-surface from the centre and is  $\sim 10^{-15}$  cm. in the case of radioactive elements. It may be looked upon as a surface separating the region (core) where there is no electric field, from the region (shell) where the electric field is Coulombian. So it must be considered an important limiting surface within any nucleus, *not necessarily radioactive*. It is also confirmed by the wave-statistical theory, since formula (8) is unaffected even if the damping coefficient be  $b=0$ . Now, in lighter elements the core is not very dense, so that  $b=0$ , and there is no spontaneous transmutation. In this case, since from (8)  $r_0$  is inversely proportional to the atomic number, it should have a larger value, viz.,  $r_0 \sim 10^{-14}$  cm.; consequently the neutral shell becomes thinner. It is interesting to note that for hydrogen ( $z=1$ ),  $r_0$  according to (8) is  $\sim 10^{-13}$  cm., which is the order of the proton-radius. It also agrees, as it should, with the order of  $r_1$  the radius of emission. It is now sufficiently clear that, apart from the question of disintegration, formula (8) deduced from the boundary conditions is of general validity and gives the radius of the spherical distribution of charge in the nucleus.

Physical Laboratory, Presidency  
College, Calcutta, India.  
August 1935.

† Born, *Zeits. f. Phys.* lviii. p. 306 (1929).

‡ Sexl, *Zeits. f. Phys.* liv. p. 445 (1929); lvi. p. 62 (1929).

§ Sexl, *Zeits. f. Phys.* lxxxvii. p. 105 (1934).

LXXXVIII. *Atomic Weights by Calculation.*  
*By A. COLIN WOODMANSEY \*.*

THE development of our knowledge of atomic structure is marked by a series of attempts to assert, disprove, and explain divergences from the "whole number rule."

Prout relegated the differences between atomic weights and whole number multiples of that of hydrogen to discrepancies in experimental determination, and this view was held until Stas developed his technique to a degree of accuracy which left no doubt that atomic weights were not whole numbers.

A satisfactory explanation of such atomic weights as that of chlorine, which differed from the nearest whole number by more than 1 per cent., was then afforded by the discovery of isotopes, and was followed by a revival of Prout's hypothesis. Experimental determinations, however, were becoming increasingly accurate, and it was shown beyond doubt that the atomic weights of some simple elements differed from the nearest whole number by nearly 0·1 per cent. (and that of hydrogen by nearly 1 per cent.).

In the absence of any other explanation this difference has been imputed to energy considerations, but the following method provides calculated atomic weights which agree closely with those experimentally determined (and hence satisfactorily explains divergences from the whole number rule) without having recourse to energy factors.

Let us assume that the atom of any element consists of a nucleus of  $x$  neutrons and  $y$  positrons, surrounded by  $y$  orbital negatrons ( $x$ =mass no.,  $y$ =atomic no.), and that energy changes do not affect its weight. Then if  $n$  represent the weight of a neutron and  $E$  the sum of the weights of one negatron and one positron we may write

$$\text{atomic weight} = xn + yE. \quad \dots \quad (1)$$

Now by using the known data for two simple elements (or pure isotopes) simultaneous equations may be

\* Communicated by the Author.

obtained, and solved to give values for  $n$  and  $E$ . For example,

$${}^7\text{N}^{14} = 14n + 7E = 14 \cdot 007,$$

$${}_{53}\text{I}^{127} = 127n + 53E = 126 \cdot 917;$$

$$\therefore n = .9935 \text{ and } E = .0140.$$

This process was repeated for various pairs of elements, and the resultant values were in close agreement. The

Element.	Standard atomic weight.	Calcd. atomic wt. ( $n = .9935$ , $E = .0140$ ).	Percentage disagreement.
1 H <sup>1</sup> .....	1.0076	1.0075	.01
2 He .....	4.002	4.002	nil.
7 N <sup>14</sup> .....	14.007	14.007	nil.
9 F .....	19.00	19.00	nil.
11 Na .....	22.997	23.005	.03
15 P .....	31.02	31.01	.03
23 V .....	50.95	50.99	.08
25 Mn .....	54.93	54.99	.11
27 Co .....	58.94	58.99	.08
33 As .....	74.91	74.97	.08
39 Yt .....	88.92	88.97	.06
41 Cb .....	92.91	92.97	.06
53 I .....	126.92	126.92	nil.
55 Cs .....	132.91	132.91	nil.
57 La .....	138.92	138.89	.02
59 Pr .....	140.92	140.91	.01
73 Ta .....	180.89	180.85	.02

atomic weights of all the simple elements were then calculated by substituting the above figures in equation 1, with results as shown in the table.

The values in the first atomic weight column are from the 1935 International Atomic Weights, except the figure for Ta, which is that given by Aston and recently confirmed by Hönigschmid. In the cases of H<sup>1</sup> and N<sup>14</sup> suitable corrections were made for the presence of the higher isotopes.

Al and In have not been used as it is not certain that they consist entirely of one isotope, and Sc is omitted as Aston considers the value 45.10 to be inadmissible; otherwise all simple elements are included. Complex elements other than H and N cannot be employed because the proportionate amounts of their isotopes are not known with sufficient accuracy to enable the atomic weights of these to be deduced from the standard atomic weights.

The agreement between experimental and calculated results is within the limit of experimental error (in many cases the figures show no differences whatever), and it is reasonable to suppose that when experimental values attain greater accuracy, and correspondingly accurate figures for  $n$  and E have been derived therefrom, the new calculated atomic weights will continue to agree with experimental data.

To show that these figures (·9935 and ·0140) have a real significance other values for  $n$  and E were tried, and it was found that the further they diverged from the above numbers the greater became the discrepancy between the calculated and experimental atomic weights.

An alternative deduction may be made from the above results. The value  $n$  may represent not the mass of a neutron when isolated (as this has been claimed by experimenters to exceed ·9935), but its effective mass when subject to a packing effect in the condensed system of the nucleus. The results suggest that this effect is constant for each neutron in any atom. Also the mass : weight relationship may not be the same for the different kinds of intra-atomic particle. In this case the above figures will strictly represent weights and not masses.

Whatever the explanation may be, however, it certainly appears that the weight of any atom may be represented by the expression  $xn+yE$ , where  $x$  is the mass number,  $y$  the atomic number, and  $n$  and E are constants.

The author desires to thank Dr. C. H. D. Clark and Mr. R. S. Bradley, of the Chemistry Department, for interest and advice during the preparation of this paper.

The University of Leeds.  
June 1935.

**LXXXIX.** *On Operational Representations of Confluent Hypergeometric Functions and their Integrals.* By S. C. DHAR, D.Sc., Professor of Mathematics, Nagpur, India \*.

*Introduction.*

HEAVISIDE'S operational method is a powerful instrument in exploring the properties of functions of different kind. The theory of these operators has been clarified first by Bromwich and its use extended by other workers in the field. A general account of these is given by Jeffreys †, in whose tract many references will be found.

Recently Van der Pol ‡ has given a method by which linear differential equations with variable coefficients can be solved by the operational method. By applying it to Bessel's differential equation he showed how it would enable us to obtain easily many of the known properties of that function and also to obtain new ones. More recently Goldstein § has obtained operational representations of Whittaker's and Weber's functions.

In the present paper it is my object to obtain operational representation of confluent hypergeometric functions by the method of Van der Pol, in terms of hypergeometric functions, and from the known properties of the latter to obtain several relations and integrals of the former.

1. A given function  $h(x)$  is said to be operationally represented by another function  $f(p)$ , called "the image," if they satisfy Carson's integral ||

$$f(p) = p \int_0^{\infty} e^{-px} h(x) dx, \quad . . . . \quad (1)$$

provided the integral converges.

The relation (1) between  $h(x)$  and  $f(p)$  may be denoted, following Van der Pol, as

$$f(p) \doteq h(x) \quad \text{or} \quad \text{by } h(x) \doteq f(p), \quad . . . . \quad (2)$$

\* Communicated by the Author.

† "Operational Methods in Mathematical Physics." (Cambridge Tract, No. 23.)

‡ Van der Pol, Phil. Mag. viii. pp. 861-898 (1929).

§ Goldstein, Proc. Lond. Math. Soc. 2, xxxiv. pp. 103-125 (1932).

|| Carson, 'Electric Circuit Theory and Operational Calculus' (1926).

both meaning that  $h(x)$  transformed operationally gives  $f(p)$ , and  $f(p)$  interpreted backwards gives  $h(x)$ .

When  $f(p)$  is known and  $f(p)/p$  is an analytic function of the complex variable  $p$ , then by means of Bromwich-Wagner theorem, we get back  $h(x)$  as

$$h(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{f(p)}{p} e^{px} dp, \text{ where } c > 0, \quad (3)$$

which follows from the Mellin-Fourier theorem\*.

Thus if  $h(x)=x$ , then  $f(p)=\frac{1}{p}$ , which is operationally represented by

$$\frac{1}{p} \doteqdot x \quad \text{or} \quad x \doteqdot \frac{1}{p}.$$

In fact, we have the relation

$$\frac{1}{p^n} \doteqdot \frac{x^n}{\Gamma(1+n)}. \quad \dots \dots \dots \quad (4)$$

Now, from the above definition of operational representation, a set of theorems was derived by Carson and a few more added later on by Van der Pol and K. F. Niessen†. As we shall make frequent use of some of these relations, they are summarized here without proof.

### Fundamental Rules.

If  $f(p) \doteqdot h(x)$ , then we shall have

$$f\left(\frac{p}{s}\right) \doteqdot h(sx), \text{ if } s \text{ is constant and } > 0. \quad (5)$$

$$pf(p) \doteqdot \frac{d}{dx} h(x), \quad \text{if } h(0)=0. \quad \dots \dots \quad (6)$$

$$\left(-p \frac{d}{dp}\right)^n f(p) \doteqdot \left(x \frac{d}{dx}\right)^n h(x), \quad n > 0. \quad \dots \dots \quad (7)$$

$$p\left(-\frac{d}{dp}\right)^n \frac{f(p)}{p} \doteqdot x^n h(x), \quad n > 0. \quad \dots \dots \quad (8)$$

$$\frac{p}{p+\alpha} f(p+\alpha) \doteqdot e^{-\alpha x} h(x). \quad \dots \dots \quad (9)$$

\* Courant und Hilbert, 'Methoden der Mathematischen Physik,' i. p. 90.

† Van der Pol and Niessen, Phil. Mag. xi. pp. 537-577 (1932).

$$\int_0^\infty \frac{pf(p)}{p} dp \doteq \int_x^\infty \frac{h(x)}{x} dx. \quad \dots \quad (10)$$

$$\int_p^\infty \frac{f(p)}{p} dp \doteq \int_0^x \frac{h(x)}{x} dx. \quad \dots \quad (11)$$

2. Consider the well-known differential equation

$$\frac{d^2y}{dx^2} + \frac{dy}{dx} + \left( \frac{k}{x} + \frac{\frac{1}{4} - m^2}{x^2} \right) y = 0, \quad \dots \quad (12)$$

whose solution is given by  $y = e^{-\frac{1}{2}x} W_{k,m}(x)$ , where  $W$  is the Whittaker's function.

Transform it by the substitution

$$u = x^{l-1} y,$$

and we get

$$x^2 \frac{d^2u}{dx^2} + \{x - 2(l-1)\} x \frac{du}{dx} + \{l(l-1) + (k-l+1)x + (\frac{1}{4} - m^2)\} u = 0.$$

Multiply it by  $e^{-px}$  and integrate between 0 and  $\infty$ , and putting

$$X = \int_0^\infty e^{-px} u(x) dx,$$

we get on integration by parts and simplification

$$p(p+1) \frac{d^2X}{dp^2} + \{(l-k+1) + 2(l+1)p\} \frac{dX}{dp} + (l^2 + l + \frac{1}{4} - m^2) X = 0. \quad (13)$$

This equation is of the hypergeometric type whose solutions are given by

$$\left. \begin{aligned} (\alpha) \quad P &\equiv {}_2F_1(l+m+\tfrac{1}{2}, l-m+\tfrac{1}{2}; l-k+1; -p) \\ Q &\equiv (-p)^{(k-l)} {}_2F_1(m+k+\tfrac{1}{2}, k-m+\tfrac{1}{2}; k-l+1; -p), \end{aligned} \right\}. \quad (14)$$

valid near the origin.

$$\left. \begin{aligned} (\beta) \quad R &\equiv (-p)^{-(l+m+\tfrac{1}{2})} {}_2F_1\left(l+m+\tfrac{1}{2}, k+m+\tfrac{1}{2}; 2m+1; -\frac{1}{p}\right) \\ S &\equiv (-p)^{-(l-m+\tfrac{1}{2})} {}_2F_1\left(l-m+\tfrac{1}{2}, k-m+\tfrac{1}{2}; -2m+1; -\frac{1}{p}\right). \end{aligned} \right\}. \quad (15)$$

valid at infinity.

The following relations are found to exist between these solutions, valid in a certain region :—

$$\begin{aligned} P &= \frac{\Gamma(l-k+1)\Gamma(-2m)}{\Gamma(l-m+\frac{1}{2})\Gamma(-m-k+\frac{1}{2})} e^{i\pi(l+m+\frac{1}{2})} R \\ &\quad + \frac{\Gamma(l-k+1)\Gamma(2m)}{\Gamma(l+m+\frac{1}{2})\Gamma(m-k+\frac{1}{2})} e^{i\pi(l-m+\frac{1}{2})} S. \end{aligned} \quad (16)$$

$$\begin{aligned} e^{-i\pi(k-l)}. Q &= \frac{\Gamma(-2m)\Gamma(k-l+1)}{\Gamma(-l-m+\frac{1}{2})\Gamma(k-m+\frac{1}{2})} e^{i\pi(l+m+\frac{1}{2})} R \\ &\quad + \frac{\Gamma(2m)\Gamma(k-l+1)}{\Gamma(-l+m+\frac{1}{2})\Gamma(k+m+\frac{1}{2})} e^{i\pi(l-m+\frac{1}{2})} S. \end{aligned} \quad (17)$$

Hence for some particular values of the constants A and B, we must have

$$\begin{aligned} x^{l-1} e^{-\frac{1}{2}x} W_{k,m}(x) &\doteqdot A p(-p)^{-(l+m+\frac{1}{2})} {}_2F_1\left(l+m+\frac{1}{2},\right. \\ &\quad \left.k+m-\frac{1}{2}; 2m+1; -\frac{1}{p}\right) \\ &\quad + B p(-p)^{-(l-m+\frac{1}{2})} {}_2F_1\left(l-m+\frac{1}{2}, k-m+\frac{1}{2};\right. \\ &\quad \left.-2m+1; -\frac{1}{p}\right), \end{aligned} \quad (18)$$

which by rule (9) becomes

$$\begin{aligned} x^{l-1} W_{k,m}(x) &\doteqdot A p(\frac{1}{2}-p)^{-(l+m+\frac{1}{2})} {}_2F_1\left(l+m+\frac{1}{2},\right. \\ &\quad \left.k+m+\frac{1}{2}; 2m+1; \frac{1}{\frac{1}{2}-p}\right) \\ &\quad + B p(\frac{1}{2}-p)^{-(l-m+\frac{1}{2})} {}_2F_1\left(l-m+\frac{1}{2}, k-m+\frac{1}{2};\right. \\ &\quad \left.-2m+1; \frac{1}{\frac{1}{2}-p}\right). \end{aligned} \quad (19)$$

It is easy to see that by (4) and (9)

$$\begin{aligned} p(\frac{1}{2}-p)^{-(l+m+\frac{1}{2})} {}_2F_1\left(l+m+\frac{1}{2}, k+m+\frac{1}{2}; 2m+1; \frac{1}{\frac{1}{2}-p}\right) \\ \stackrel{?}{=} \frac{x^{l-1}}{\Gamma(l+m+\frac{1}{2})} (-)^{-(l+2m+1)} M_{-k, m}(-x)^*. \quad (20) \end{aligned}$$

and

$$\begin{aligned} p(\frac{1}{2}-p)^{-(l-m+\frac{1}{2})} {}_2F_1\left(l-m+\frac{1}{2}, k-m+\frac{1}{2}; -2m+1; \frac{1}{\frac{1}{2}-p}\right) \\ \stackrel{?}{=} \frac{x^{l-1}}{\Gamma(l-m+\frac{1}{2})} (-)^{-(l-2m+1)} M_{-k, -m}(-x)^*. \quad (21) \end{aligned}$$

Hence from the definition of the function  $W_{k, m}(x)$ , we obtain

$$\begin{aligned} A = \frac{\Gamma(-2m)\Gamma(l+m+\frac{1}{2})}{\Gamma(-m-k+\frac{1}{2})} e^{i\pi(l+m+\frac{1}{2})} \\ \text{and} \quad B = \frac{\Gamma(2m)\Gamma(l-m+\frac{1}{2})}{\Gamma(m-k+\frac{1}{2})} e^{i\pi(l-m+\frac{1}{2})}. \quad (22) \end{aligned}$$

Hence from (18) and (16) we obtain

$$\begin{aligned} & \frac{\Gamma(l-k+1)}{\Gamma(l+m+\frac{1}{2})\Gamma(l-m+\frac{1}{2})} x^{l-1} e^{-\frac{1}{2}x} W_{k, m}(x) \\ & \stackrel{?}{=} p {}_2F_1(l+m+\frac{1}{2}, l-m+\frac{1}{2}; l-k+1; -p). \quad (23) \end{aligned}$$

Cf. Goldstein, loc. cit. p. 119.

Therefore by (1)

$$\begin{aligned} \int_0^\infty x^{l-1} e^{-(p+\frac{1}{2})x} W_{k, m}(x) dx &= \frac{\Gamma(l+m+\frac{1}{2})\Gamma(l-m+\frac{1}{2})}{\Gamma(l-k+1)} \\ &\times {}_2F_1(l+m+\frac{1}{2}, l-m+\frac{1}{2}; l-k+1; -p). \quad (24) \end{aligned}$$

We obtain another form of  $W_{k, m}(x)$ . We get from (18) and (22)

$$\begin{aligned} x^{l-1} e^{-\frac{1}{2}x} W_{k, m}(x) &\stackrel{?}{=} p \left\{ \frac{\Gamma(-2m)\Gamma(l+m+\frac{1}{2})}{\Gamma(-m-k+\frac{1}{2})} e^{i\pi(l+m+\frac{1}{2})} R \right. \\ &\quad \left. + \frac{\Gamma(2m)\Gamma(l-m+\frac{1}{2})}{\Gamma(\frac{1}{2}+m-k)} e^{i\pi(l-m+\frac{1}{2})} S \right\}. \end{aligned}$$

But from the well-known relation

$$\Gamma(z)\Gamma(1-z) = \frac{\pi}{\sin \pi z}$$

\*  $M_{k, m}$  defined in Whittaker and Watson's 'Modern Analysis,' pp. 338-339 (1927). This work will in future be referred to as M. A.

NOTE.—The properties of these functions are being investigated in a separate paper.

we obtain on simplification and from the relation (17)

$$x^{l-1}e^{-\frac{1}{2}x}W_{k,m}(x) \doteq \frac{\Gamma(m+k+\frac{1}{2})\Gamma(-m+k+\frac{1}{2})}{\Gamma(k-l+1)} p(-p)^{k-l} \\ \times {}_2F_1(m+k+\frac{1}{2}, k-m+\frac{1}{2}; k-l+1; -p), \quad (25)$$

whence we get the integral

$$\int_0^\infty x^{l-1}e^{-(p+\frac{1}{2})x}W_{k,m}(x)dx \\ \cdot \frac{\Gamma(\frac{1}{2}+m+k)\Gamma(-m+k+\frac{1}{2})}{\Gamma(k-l+1)} (-p)^{k-l} \\ \times {}_2F_1(m+k+\frac{1}{2}, k-m+\frac{1}{2}; k-l+1; -p). \quad (26)$$

3. We now investigate some of the properties of the function by the help of (23) or (25).

From the property of the hypergeometric function  ${}_2F_1$ , it is easy to see from (23) or (25) that

$$W_{k,m}(x) = W_{k,-m}(x).$$

Next we find the recurrence formulæ by using the fundamental rule (6). For this we write (23) in the form

$$x^{l-1}e^{-\frac{1}{2}x}W_{k,m}(x) \doteq \frac{\Gamma\alpha\Gamma\beta}{\Gamma\gamma} p {}_2F_1(\alpha, \beta; \gamma; -p), \quad (23)$$

where  $\alpha=l+m+\frac{1}{2}$ ,  $\beta=l-m+\frac{1}{2}$ , and  $\gamma=l-k+1$ .

Hence by rule (6) we have

$$\frac{d}{dx} \left\{ x^{l-m} e^{-\frac{1}{2}x} W_{k,m}(x) \right\} \doteq \frac{\Gamma\alpha\Gamma\beta}{\Gamma\gamma} p {}_2F_1(\alpha, \beta; \gamma; -p).$$

But

$${}_2F_1(\alpha, \beta+1; \gamma; z) - {}_2F_1(\alpha, \beta; \gamma; z) \\ = \frac{\alpha z}{\gamma} {}_2F_1(\alpha+1, \beta+1; \gamma+1; z). \quad (27)$$

Hence we obtain

$$\frac{d}{dx} \left\{ x^{l-1} e^{-\frac{1}{2}x} W_{k,m}(x) \right\} = -x^{l-\frac{3}{2}} e^{-\frac{1}{2}x} W_{k+\frac{1}{2}, m-\frac{1}{2}}(x) \\ + (l-m-\frac{1}{2})x^{l-2} e^{-\frac{1}{2}x} W_{k,m}(x),$$

that is

$$xW'_{k,m}(x) = (\frac{1}{2}-m+\frac{1}{2}x)W_{k,m}(x) - x^{\frac{1}{2}}W_{k+\frac{1}{2}, m-\frac{1}{2}}(x). \quad (28)$$

But if we apply rule (7) when  $n=1$  to (25), we obtain on reduction by (27) and (25)

$$x \frac{d}{dx} \left\{ x^{l-1} e^{-\frac{1}{2}x} W_{k,m}(x) \right\} = -(k-l+1)x^{l-1} e^{-\frac{1}{2}x} W_{k,m}(x) \\ - x^{l-1} e^{-\frac{1}{2}x} W_{k+1,m}(x),$$

that is

$$xW'_{k,m}(x) = (\frac{1}{2}x - k)W_{k,m}(x) - W_{k+1,m}(x). \quad \dots \quad (29)$$

From (28) and (29) it is now easy to obtain the relation  
 $W_{k,m}(x) = x^{\frac{1}{2}}W_{k-\frac{1}{2},m-\frac{1}{2}}(x) + (\frac{1}{2} - k + m)W_{k-1,m}(x). \quad (30)$

The relations (28), (29), and (30) are equivalent to the known recurrence-formulæ (see M. A., p. 352, Ex. 3).

4. We proceed to obtain a few more relations and integrals.

From the following relations \* between hypergeometric functions

$$\begin{aligned} {}_2F_1(\alpha, \beta; \gamma; z) &= (1-z)^{-\alpha} {}_2F_1\left(\alpha, \gamma-\beta; \gamma; \frac{z}{z-1}\right) \\ &= (1-z)^{-\beta} {}_2F_1\left(\beta, \gamma-\alpha; \gamma; \frac{z}{z-1}\right), \end{aligned}$$

we obtain from (23)

$$\begin{aligned} x^{l-1}e^{-\frac{1}{2}x}W_{k,m}(x) &\doteq \frac{\Gamma\alpha\Gamma\beta}{\Gamma\gamma} p(1+p)^{-\alpha} \\ &\times {}_2F_1\left(\alpha, \gamma-\beta; \gamma; \frac{p}{p+1}\right). \end{aligned} \quad (31)$$

Now, on applying rule (9), it becomes

$$\begin{aligned} x^{-1}e^{-\frac{1}{2}x}W_{k,m}(x) &\doteq \frac{\Gamma\alpha\Gamma\beta}{\Gamma\gamma} (p)^{-\alpha+1} \\ &\times {}_2F_1\left(\alpha, \gamma-\beta; \gamma; 1-\frac{1}{p}\right); \end{aligned} \quad (32)$$

whence by (1),

$$\begin{aligned} \int_0^\infty x^{l-1}e^{-(p-\frac{1}{2})x}W_{k,m}(x)dx &= \frac{\Gamma(l+m+\frac{1}{2})\Gamma(l-m+\frac{1}{2})}{\Gamma(l-k+1)} \\ &\times (p)^{-(l+m+\frac{1}{2})} {}_2F_1\left(l+m+\frac{1}{2}, l-m+\frac{1}{2}; l-k+1; 1-\frac{1}{p}\right), \\ &\dots \end{aligned} \quad (33)$$

which holds when  $l-k+1>0$ .

If instead we take the relation (25) and apply a similar known transformation † to the integral Q, viz.,

$$Q \equiv (-p)^{k-l}(1+p)^{-(\frac{1}{2}+m+k)} {}_2F_1\left(\frac{1}{2}+m+k, \frac{1}{2}-l+m; k-l+1; \frac{p}{p+1}\right),$$

\* Barnes, Proc. Lond. Math. Soc. (2) vi. pp. 141-177.

† Barnes, loc. cit.

we get, similarly,

$$\begin{aligned} x^{l-1} e^{-\frac{1}{2}x} W_{k,m}(x) &\doteq \frac{\Gamma(\frac{1}{2}+m+k)\Gamma(\frac{1}{2}-m+k)}{\Gamma(k-l+1)} p(-p)^{k-l} \\ &\times (1+p)^{-(\frac{1}{2}+m+k)} {}_2F_1\left(\frac{1}{2}+m+k, \frac{1}{2}-l+m; k-l+1; \frac{p}{p+1}\right). \end{aligned} \quad (34)$$

and

$$\begin{aligned} x^{l-1} e^{\frac{1}{2}x} W_{k,m}(x) &\doteq \frac{\Gamma(\frac{1}{2}+m+k)\Gamma(\frac{1}{2}-m+k)}{\Gamma(k-l+1)} p^{\frac{1}{2}-m-k} \\ &\times (1-p)^{k-l} {}_2F_1\left(\frac{1}{2}+m+k, \frac{1}{2}-l+m; k-l+1; 1-\frac{1}{p}\right), \end{aligned} \quad (35)$$

the latter gives the integral

$$\begin{aligned} \int_0^\infty x^{l-1} e^{-(p-\frac{1}{2})x} W_{k,m}(x) dx \\ = \frac{\Gamma(\frac{1}{2}+m+k)\Gamma(\frac{1}{2}-m+k)}{\Gamma(k-l+1)} p^{-\frac{1}{2}-m-k} (1-p)^{k-l} \\ \times {}_2F_1\left(\frac{1}{2}+m+k, \frac{1}{2}-l+m; k-l+1; 1-\frac{1}{p}\right), \end{aligned} \quad (36)$$

which holds when  $k-l+1>0$ .

In (35) if we put  $l=-m+\frac{1}{2}$ , and simplify, we obtain

$$x^{-m-\frac{1}{2}} e^{\frac{1}{2}x} W_{k,m}(x) \doteq \Gamma(\frac{1}{2}-m+k) p^{\frac{1}{2}+m-k} (1-p)^{k+m-\frac{1}{2}}, \quad \dots \quad (37)$$

which by (3) and after deformation of the contour, reduces to the form

$$\begin{aligned} x^{-m-\frac{1}{2}} e^{\frac{1}{2}x} W_{k,m}(x) &= -\frac{\Gamma(\frac{1}{2}-m+k)}{2\pi i} \\ &\times \int_{-\infty}^{(0+)} e^{-px} (-p)^{m-k-\frac{1}{2}} (1+p)^{k+m-\frac{1}{2}} dp, \end{aligned} \quad (38)$$

provided  $\frac{1}{2}-m+k$  is not a negative integer \*.

5. We proceed to obtain an extended Barnes's form of  $W$  function. From (23) we obtain by (3)

$$\begin{aligned} x^{l-1} e^{-\frac{1}{2}x} W_{k,m}(x) &= \frac{1}{2\pi i} \frac{\Gamma(l+m+\frac{1}{2})\Gamma(l-m+\frac{1}{2})}{\Gamma(l-k+1)} \\ &\int_{c-i\infty}^{c+i\infty} e^{px} {}_2F_1(l+m+\frac{1}{2}, l-m+\frac{1}{2}; l-k+1; -p) dp. \end{aligned}$$

\* M. A., Art. 16.12, p. 340.

But by Barnes's integral \*

$$\frac{\Gamma(l+m+\frac{1}{2})\Gamma(l-m+\frac{1}{2})}{\Gamma(l-k+1)} {}_2F_1(l+m+\frac{1}{2}, l-m+\frac{1}{2}; l-k+1, -p) \\ = -\frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \frac{\Gamma(l+m+\frac{1}{2}+s)\Gamma(l-m+\frac{1}{2}+s)\Gamma(-s)}{\Gamma(l-k+1+s)} (p)^s ds,$$

where  $|\arg p| < \pi \dots \dots \quad (39)$

$$= -\frac{1}{2\pi i} \frac{1}{\Gamma(\frac{1}{2}-k-m)\Gamma(\frac{1}{2}-k+m)} \\ \int_C \Gamma(s)\Gamma(s-k-l)\Gamma(l+m+\frac{1}{2}-s)\Gamma(l-m+\frac{1}{2}-s)(1+p)^{-s} ds, \dots \dots \quad (40)$$

where  $C$  is the contour parallel to the imaginary axis and passes between the sequences of positive and negative poles of the subject of integration, where  $|\arg(1+p)| > 2\pi$  which can always be satisfied, and where  $k \pm m + \frac{1}{2}$  are not positive integers.

Hence we get

$$x^{l-1} e^{-\frac{1}{2}x} W_{k,m}(x) = -\frac{1}{2\pi i} \frac{1}{\Gamma(\frac{1}{2}-k-m)\Gamma(\frac{1}{2}-k+m)} \\ \int_{c-i\infty}^{c+i\infty} e^{px}(1+p)^{-s} dp \int_C \Gamma(s)\Gamma(s-k-l)\Gamma(l+m+\frac{1}{2}-s) \\ \times \Gamma(l-m+\frac{1}{2}-s) ds. \dots \dots \quad (41)$$

But

$$-\frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{px}(1+p)^{-s} dp = e^{-x} \frac{x^{s-1}}{\Gamma s}. \dots \dots \quad (42)$$

Hence from (41) and (42) we get

$$W_{k,m}(x) = \frac{x^{-l} e^{-\frac{1}{2}x}}{\Gamma(\frac{1}{2}-k-m)\Gamma(\frac{1}{2}-k+m)} \cdot \frac{1}{2\pi i} \\ \int_{-i\infty}^{i\infty} \Gamma(s-k-l)\Gamma(l+m+\frac{1}{2}-s)\Gamma(l-m+\frac{1}{2}-s)x^s ds, \quad (43)$$

provided  $|\arg x| < \frac{3\pi}{2}$  in order that the integral may be analytic.

\* Barnes, loc. cit. pp. 156-157; M. A., p. 286.

A special form of the above is obtained by taking  $l=-k$ , when we get

$$\begin{aligned} W_{k,m}(x) &= \frac{x^k e^{-\frac{1}{2}x}}{\Gamma(\frac{1}{2}-k-m)\Gamma(\frac{1}{2}-k+m)} \frac{1}{2\pi i} \\ &\quad \int_{-i\infty}^{i\infty} \Gamma(s)\Gamma(-k+m+\frac{1}{2}-s)\Gamma(-k-m+\frac{1}{2}-s)x^s ds. \quad (44) \end{aligned}$$

An integral of Mellin-Barnes type \*.

Again, if we put  $l=0$ , we get

$$\begin{aligned} W_{k,m}(x) &= \frac{e^{-\frac{1}{2}x}}{\Gamma(\frac{1}{2}-k-m)\Gamma(\frac{1}{2}-k+m)} \frac{1}{2\pi i} \\ &\quad \times \int_{-i\infty}^{i\infty} \Gamma(s-k)\Gamma(m+\frac{1}{2}-s)\Gamma(-m+\frac{1}{2}-s)x^s ds. \quad (45) \end{aligned}$$

Again, from (39) we can get

$$\begin{aligned} x^l e^{-\frac{1}{2}x} W_{k,m}(x) \\ = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \frac{\Gamma(l+m+\frac{1}{2}-s)\Gamma(l-m+\frac{1}{2}-s)}{\Gamma(l-k+1-s)} x^s ds. \quad (46) \end{aligned}$$

6. We proceed to consider particular forms of the operational representation of the W function to get new relations of the function.

In (34) take  $l=-m+\frac{1}{2}$  and apply rule (5) when  $u>0$ , we get

$$\begin{aligned} \left(\frac{x}{u}\right)^{-m-\frac{1}{2}} e^{-\frac{1}{2}x} W_{k,m}\left(\frac{x}{u}\right) \\ \stackrel{?}{=} -\Gamma(\frac{1}{2}-m+k)(pu+1)^{m-k-\frac{1}{2}}(-pu)^{m+k-\frac{1}{2}}, \\ \stackrel{?}{=} -\Gamma(\frac{1}{2}-m+k)(-pu)^{m+k-\frac{1}{2}}\{p(u-1)+(p+1)\}^{m-k-\frac{1}{2}} \end{aligned}$$

which, on expansion and simplification, gives the relation

$$u^{-k} e^{\frac{1}{2}x} \left(1 - \frac{1}{u}\right) W_{k,m}\left(\frac{x}{u}\right) = \sum_{r=0}^{\infty} \frac{(u-1)^r}{r!} W_{k+r,m}(x). \quad (47)$$

*Cf.* Goldstein.

If instead, we start with (37) and proceed as above, we obtain

$$\begin{aligned} u^k e^{\frac{1}{2}x} \left(\frac{1}{u}-1\right) W_{k,m}\left(\frac{x}{u}\right) &= W_{k,m}(x) \\ + \sum_{r=1}^{\infty} \frac{\{(k-\frac{1}{2})^2-m^2\}\{(k-\frac{3}{2})^2-m^2\}\dots\{(k-r+\frac{1}{2})^2-m^2\}}{r!} \\ &\quad \times (1-u)^r W_{k-r,m}(x). \quad (48) \end{aligned}$$

\* Cf. M. A., pp. 343-345.

In (35), put  $l=m+\frac{1}{2}$  and  $k=s+m+\frac{1}{2}$ , we get on simplification,

$$x^{m-\frac{1}{2}} e^{\frac{1}{2}x} W_{s+m+\frac{1}{2}, m}(x) \doteqdot \Gamma(2m+s+1) \left(\frac{1}{p}-1\right)^s p^{-2m}, \quad (49)$$

whence by rule (5),

$$u^{m+s+\frac{1}{2}} e^{\frac{1}{2}x} \left(\frac{1}{u}-1\right) W_{s+m+\frac{1}{2}, m}\left(\frac{x}{u}\right) = \Gamma(2m+s+1)(1-u)^s$$

$$\left\{ W_{m+\frac{1}{2}, m}(x) + \sum_{r=1}^{\infty} \frac{s(s-1)\dots(s-r+1)}{r!} \right.$$

$$\left. \times \frac{(1-u)^{-r}}{\Gamma(2m+r+1)} W_{r+m+\frac{1}{2}, m}(x) \right\}, \quad (50)$$

where  $s$  is any number.

From the differential equation it is easy to get

$$\int_0^\infty W_{r+m+\frac{1}{2}, m}(x) W_{n+m+\frac{1}{2}, m}(x) \frac{dx}{x} = 0$$

(when  $r \neq n$  and  $m > -\frac{1}{2}$ ),

$$= \Gamma(r+1) \Gamma(2m+r+1) \quad (\text{when } r=n).$$

Hence from (50) we get

$$\int_0^\infty e^{\frac{1}{2}x} \left(\frac{1}{u}-1\right) W_{s+m+\frac{1}{2}, m}\left(\frac{x}{u}\right) W_{r+m+\frac{1}{2}, m}(x) \frac{dx}{x}$$

$$= \Gamma(2m+s+1) \Gamma(2m+r+1) \cdot \{s(s-1)\dots(s-r+1)\}$$

$$\times \frac{(1-u)^{s-r}}{u^{m+s+\frac{1}{2}}}, \quad . \quad (51)$$

where  $r$  is a positive integer and  $s$ , if a positive integer, must be greater than  $r$ .

7. After having obtained different forms of operational representation of the function, we now consider some examples of the application of the rules to obtain relations of  $W$  functions connected with other functions.

(i.) In (23) take  $k=-\frac{1}{2}$ ,  $l=\frac{1}{2}$ ,  $m=0$ , and we get

$$x^{-\frac{1}{2}} e^{-\frac{1}{2}x} W_{-\frac{1}{2}, 0}(x) \doteqdot \log(1+p).$$

Now by rule (10), we obtain from the known relations

$$\frac{p}{p+1} \doteqdot e^{-x}$$

the relation

$$Ei(x) \equiv \int_x^\infty \frac{e^{-x}}{x} dx \doteqdot \log(1+p).$$

Therefore

$$Ei(x) = x^{-\frac{1}{2}} e^{-\frac{1}{2}x} W_{-\frac{1}{2}, 0}(x). \quad . . . \quad (52)$$

(ii.) In (23) by application of rule (9) we get

$$\begin{aligned} x^{l-1} W_{k, m}(x) &\doteq \frac{\Gamma(l+m+\frac{1}{2}) \Gamma(l-m+\frac{1}{2})}{\Gamma(l-k+1)} p_2 F_1 \\ &\quad \times (l+m+\frac{1}{2}, l-m+\frac{1}{2}; l-k+1; \frac{1}{2}-p). \end{aligned}$$

Now apply rule (5) and put  $k=0$ ,  $l=0$ , and  $m=n+\frac{1}{2}$ , we get

$$\begin{aligned} (2x)^{-1} W_{0, n+\frac{1}{2}}(2x) &\doteq -\frac{\pi}{2 \sin n\pi} p_2 F_1(n+1, -n; 1; \\ &\quad \frac{1}{2}-\frac{1}{2}p), \\ &\doteq -\frac{\pi}{2 \sin n\pi} p P_u(p), \text{ by Murphy's form.} \quad (53) \end{aligned}$$

Hence we get

$$\int_0^\infty e^{-\mu x} W_{0, n+\frac{1}{2}}(2x) \frac{dx}{x} = -\frac{\pi}{\sin n\pi} P_n(\mu). \quad . \quad (54)$$

(iii.) Defining the  $k$ -function\* as the solution of the differential equation

$$x \frac{d^2y}{dx^2} = (x-n)y.$$

We find †

$$k_{2n}(x) \doteq \frac{2p(1-p)^{n-1}}{(1+p)^{n+1}} \quad . \quad . \quad . \quad . \quad . \quad (55)$$

In (35) put  $k=n-\frac{m}{2}$ ,  $m=\frac{1}{2}-\frac{m}{2}$ ,  $l=\frac{1}{2}-\frac{m}{2}$ , and apply rule (5) taking  $s=2$ , and we get

$$2^{\frac{m}{2}} x^{-\frac{m}{2}} e^x W_{n-\frac{m}{2}, \frac{1}{2}-\frac{m}{2}}(2x) \doteq 2\Gamma(1+n-m)(2-p)^{n-1} p^{m-n}.$$

Hence on applying rule (6) and (9) to (55), we obtain

$$\begin{aligned} 2^{\frac{m}{2}} x^{-\frac{m}{2}} e^x W_{n-\frac{m}{2}, \frac{1}{2}-\frac{m}{2}}(2x) \\ = \Gamma(1+n-m) \frac{d^m}{dx^m} \{e^x k_{2n}(x)\}. \quad (56) \end{aligned}$$

\* Bateman, Proc. Nat. Acad. of Sciences, xvii. p. 689 (3) (1931).

† Shastri, Phil. Mag. xx. p. 468 (1935).

from which we obtain by Taylor's theorem

$$k_{2n}(x+h) = \sum_{m=0}^{\infty} \frac{e^{-h} h^m}{\Gamma(1+m)} 2^{\frac{m}{2}} x^{-\frac{m}{2}} W_{n-\frac{m}{2}, \frac{1}{2}-\frac{m}{2}}(2x). \quad (57)$$

Also from the following relation between the two functions \*

$$\Gamma(1+n) k_{2n}(x) = W_{n, \frac{1}{2}}(2x),$$

we can obtain from (47) and (48) the following relations:—

$$u^{-n} e^{x(1-\frac{1}{u})} k_{2n}\left(\frac{x}{u}\right) = \sum_{r=0}^{\infty} \frac{\Gamma(1+n+r)}{\Gamma(1+r)\Gamma(1+n)} (u-1)^r k_{2n+2r}(x), \quad \dots \quad (58)$$

$$u^n e^{x(\frac{1}{u}-1)} k_{2n}\left(\frac{x}{u}\right) = \sum_{r=0}^{\infty} \frac{\Gamma(1-n+r)}{\Gamma(1+r)\Gamma(1-n)} (u-1)^r k_{2n-2r}(x), \quad \dots \quad (59)$$

for all values of  $n$  and when  $u > 0$ .

(iv.) Defining Laguerre polynomial † by

$$L_s(x) = e^x \left( \frac{d}{dx} \right)^s (x^s e^{-x}),$$

we find

$$L_s(x) \doteq s! \left( 1 - \frac{1}{p} \right)^s, \text{ where } s \text{ is an integer.} \quad (60)$$

Further, if  $n$  is an integer, then

$$\ddagger L_{n+s}^n(x) = \frac{d^n}{dx^n} L_{n+s}(x) \doteq (n+s)! \left[ p^n \left( 1 - \frac{1}{p} \right)^{n+s} \right], \quad (61)$$

where [ ] means retention of negative powers of  $p$  only.

From (35) we have

$$\begin{aligned} x^{-\frac{1}{2}n-\frac{1}{2}} e^{\frac{1}{2}x} W_{\frac{1}{2}n+s+\frac{1}{2}, \frac{1}{2}n}(x) \\ \doteq \Gamma(s+1) (1-p)^{n+s} p^{-(n+s)} \\ \times {}_2F_1 \left( n+s+1, n; n+s+1; 1 - \frac{1}{p} \right), \\ \doteq \Gamma(s+1) (-)^{n+s} p^n \left( 1 - \frac{1}{p} \right)^{n+s}, \end{aligned}$$

\* Bateman, *loc. cit.*

† Courant and Hilbert, *loc. cit.* p. 77 (1924).

‡ This function multiplied by  $e^{-\frac{1}{2}x} x^{\frac{1}{2}n}$  occurs in the theory of hydrogen-like atoms in wave mechanics; see Sommerfeld, 'Atombau und spektrallinien Wellenmechanischer Ergänzungsband,' pp. 70-77 and 181-184 (1929).

$$= \frac{s!}{(n+s)!} (-)^{n+s} L_{n+s}^n(x). \quad \dots \quad (62)$$

$$= (n+s)! s! T_n^s(x), \quad \dots, \quad \dots \quad (63)$$

where  $T_n^s(x)$  is Sonine's polynomial (M.A., p. 352, Ex. 8).

When  $n=0$ , we get

$$x^{-\frac{1}{2}} e^{\frac{1}{2}x} W_{s+\frac{1}{2}, 0}(x) = (-)^s L_s(x). \quad \dots \quad (64)$$

8. The special case of the W-function in which  $m=-\frac{1}{2}$  will give us formulæ involving the parabolic cylinder functions. We consider only a few cases here.

We know\* that

$$D_n(z) = 2^{\frac{1}{2}n + \frac{1}{2}} z^{-\frac{1}{2}} W_{\frac{1}{2}n + \frac{1}{2}, -\frac{1}{2}}(\frac{1}{2}z^2). \quad \dots \quad (65)$$

Hence from (23) we get

$$2^{\frac{1}{2}-k} x^{l-\frac{1}{2}} e^{-\frac{1}{2}x} D_{2k-\frac{1}{2}}(\sqrt{2x}) \stackrel{?}{=} \frac{\Gamma(l+\frac{1}{4}) \Gamma(l+\frac{3}{4})}{\Gamma(l-k+1)} p \\ \times {}_2F_1(l+\frac{1}{4}, l+\frac{3}{4}; l-k+1; -p), \quad (66)$$

and from (32) we have

$$2^{\frac{1}{2}-k} x^{l-\frac{1}{2}} e^{\frac{1}{2}x} D_{2k-\frac{1}{2}}(\sqrt{2x}) \stackrel{?}{=} \frac{\Gamma(l+\frac{1}{4}) \Gamma(l+\frac{3}{4})}{\Gamma(l-k+1)} p^{\frac{1}{4}-l} \\ \times {}_2F_1\left(l+\frac{1}{4}, l+\frac{3}{4}; l-k+1; 1-\frac{1}{p}\right). \quad (67)$$

In the latter, take  $k=\frac{1}{2}\mu-\frac{1}{4}$ , and  $l=\frac{1}{2}\nu-\frac{1}{4}$ , and then by (1), we get on simplification, the integral †

$$\int_0^\infty z^{\nu-1} e^{(\frac{1}{2}-\alpha)z^2} D_{\mu-1}(z) dz = \frac{\pi^{\frac{1}{2}} \cdot 2^{\frac{1}{2}\mu-\nu-\frac{1}{2}}}{\alpha^{\frac{1}{2}\nu} \Gamma(\frac{1}{2}\nu-\frac{1}{2}\mu+1)} \\ \times {}_2F_1\left(\frac{1}{2}\nu, \frac{1-\mu}{2}; \frac{\nu-\mu}{2}+1; 1-\frac{1}{2\alpha}\right), \quad (68)$$

when  $\frac{\nu-\mu}{2}+1>0$ .

By (31) we will get the integral

$$\int_0^\infty z^{\nu-1} e^{-\frac{1}{2}(\alpha+\frac{1}{2})z^2} D_{\mu-1}(z) dz \\ = \frac{\pi^{\frac{1}{2}} \Gamma\nu}{\Gamma(\frac{1}{2}\nu-\frac{1}{2}\mu+1)} 2^{\frac{1}{2}\mu-\frac{1}{2}\nu-\frac{1}{2}} (1+\alpha)^{-\frac{1}{2}\nu} \\ \times {}_2F_1\left(\frac{\nu}{2}, \frac{1-\mu}{2}; \frac{\nu-\mu}{2}+1; 1-\frac{1}{\alpha+1}\right). \quad (69)$$

\* M. A., p. 342.

† Cf. Watson, Proc. Lond. Math. Soc. (2) viii. p. 400.

This reduces, on taking particular values of  $\nu$  and  $\alpha$ , to

$$(i.) \int_0^\infty z^\mu e^{-\frac{1}{4}z^2} D_{\mu-1}(z) dz = \Gamma(\mu)(\sqrt{2})^{-(\mu+2)} \sin \frac{\mu}{4}\pi, \quad \dots \quad (70)$$

$$^*(ii.) \int_0^\infty z^{\nu-1} e^{-\frac{1}{4}z^2} D_\nu(z) dz = \Gamma_\nu(\sqrt{2})^{-\nu} \sin \left( \frac{1}{2} + \frac{\nu}{4} \right). \quad \dots \quad (71)$$

The restriction in the integral (68) that  $\frac{\nu-\mu}{2}+1>0$ ,

will be removed if we consider the operational form given in (35) and substitute the values of  $l$  and  $k$  given there. We get

$$\begin{aligned} & \int_0^\infty z^{\nu-1} e^{(\frac{1}{4}-\alpha)z^2} D_{\mu-1}(z) dz \\ &= \frac{\pi^{\frac{1}{4}} \Gamma_\mu 2^{\frac{\nu-\mu-1}{2}}}{\Gamma\left(\frac{\mu-\nu}{2}+1\right) \cdot (2\alpha)^{\frac{1}{2}\mu}} (1-2\alpha)^{\frac{1}{2}(\mu-2)} \\ & \quad \times {}_2F_1\left(\frac{\mu}{2}, \frac{1-\nu}{2}; \frac{\mu-\nu}{2}+1; 1-\frac{1}{2\alpha}\right). \end{aligned} \quad (72)$$

This holds when  $\frac{\mu-\nu}{2}+1>0$ . (*Cf.* Goldstein, *loc. cit.*)

The forms corresponding to (47) and (48) are worth noting, viz.,

$$u^{-n} e^{\frac{1}{4}z^2 \left(1 - \frac{1}{u^2}\right)} D_n\left(\frac{z}{u}\right) = \sum_{r=0}^{\infty} \frac{(u^2-1)^r}{r!} D_{n+2r}(z). \quad (73)$$

(*cf.* Goldstein) and

$$\begin{aligned} \dagger u^n e^{\frac{1}{4}z^2 \left(\frac{1}{u^2}-1\right)} D_n\left(\frac{z}{u}\right) &= \sum_{r=0}^{\infty} \frac{\Gamma(n+1)}{\Gamma(n-2r+1)} \frac{(1-u^2)^r}{2^r} \\ & \quad \times D_{n-2r}(z), \end{aligned} \quad \dots \quad (74)$$

Many integrals can be obtained from these by the application of the rules of the operational calculus given before.

\* *Cf.* Watson, *loc. cit.*

† Dhar, Journ. Lond. Math. Soc. x. p. 174 (1935).

*XC. The Effect of Changes in a Torsionally Vibrating System on the Natural Frequencies of the System.*  
By W. A. TUPLIN, M.Sc.\*

In any assembly of machinery incorporating rotating parts connected by shafts or other torsionally elastic members, and subjected to fluctuating torque, resonant torsional vibrations are always a theoretical possibility. In many instances such vibrations are so small in amplitude that they have no practical importance, but in some cases dangerously high alternating torsional stresses arise if resonant vibrations are excited by sufficiently powerful harmonic components of any fluctuating torques which may be exerted on the shafts.

To guard against this possibility in the design stages the predetermination of the natural frequencies of torsional vibration becomes necessary. This may be done without determining the formal frequency equation by methods which are based on the principle of successive approximation, and which have been devised to avoid the lengthy numerical work involved in calculating the coefficients in the frequency equation by the normal algebraic methods. By the application of a special process the frequency equation can be determined, and although it is often of such high degree as to have no general solution its roots may be found if numerical values are available by using Horner's Method.

The lower natural frequencies of the system having been found the designer's problem is to ensure that the range of speed over which the machinery has to operate shall be free from "critical speeds" at which objectionally severe torsional vibrations would be produced by coincidence between a frequency of natural vibration and that of harmonic components of torques applied to the shafts. The normal procedure is to design the plant in a straightforward manner without giving any detailed consideration to its characteristics as a torsionally vibrating system, and then to calculate the lower natural frequencies. From these the more important critical speeds are easily calculated.

If a critical speed which would prove troublesome is found to lie within the range of speed covered in normal

\* Communicated by the Author.

operation it becomes necessary to make such a change in the original design as will move the critical speed out of the operating range by altering the corresponding natural frequency. This may be done (*a*) by a change in moment of inertia of one or more of the rotating masses; or (*b*) by a change in torsional stiffness of one or more of the shafts.

When such provisional changes have been made the natural frequencies must be re-calculated, and, as this is often a lengthy process, it becomes desirable to form some estimate of the effect on the natural frequency of a tentative change in inertia or stiffness. In special circumstances there is no difficulty in making such an estimate. For example, if the stiffness of *every* torsionally elastic element in the drive is multiplied by "*q*," the moments of inertia being left unaltered, the natural frequencies are multiplied by  $\sqrt{q}$ . Similarly, multiplication of *all* the moments of inertia by "*q*," with no change in stiffness, multiplies the natural frequencies by  $1/\sqrt{q}$ . In general, however, the effect of modification of stiffness or inertia of particular elements in the system is not so easily determined, but an approximate method of doing so is developed in the following analysis.

Let the vibrating system be represented by a series of rotors numbered 1, 2, 3, etc. from the extreme left, and connected by shafts similarly numbered. The moments of inertia of the rotors are denoted by  $I_1$ ,  $I_2$ ,  $I_3$ , etc. . . .  $I_{N+1}$ , and the torsional stiffnesses of the shafts by  $k_1$ ,  $k_2$ ,  $k_3$ , etc. . . .  $k_N$ . The "*r*"th shaft lies between rotors "*r*" and (*r*+1).

Let

$$k_r/I_r = a_r \quad \text{and} \quad k_r/I_{r+1} = b_r.$$

The quantities  $a_1$ ,  $b_1$ ,  $a_2$ ,  $b_2$ , etc. . . .  $a_N$ ,  $b_N$  are called the "elastic-inertia" constants of the system.

If the system is in a state of free torsional vibration the angular position of any rotor varies in simple harmonic manner expressed by

$$\theta = \lambda \sin nt,$$

where  $\theta$  = instantaneous angular displacement from an equilibrium position.

$\lambda$  = amplitude of angular vibration.

$n/2\pi$  = natural frequency with which the system is vibrating.

It may be shown that the system has  $N$  natural modes of vibration and that " $n$ " may have any one of  $N$  corresponding values. For any given value of " $n$ " the values of  $\lambda$  for the different rotors bear fixed ratios to each other, and the relative amplitudes, erected as ordinates at points representing the positions of the rotors, give the "normal elastic curve" for that particular mode of vibration.

The torques in the shafts vary harmonically in phase with the angular displacements of the rotors, and the torque amplitudes bear fixed ratios to each other.

If " $m$ " (with appropriate suffix) denote the amplitude of the torque in any shaft, we have, considering the angular acceleration of the " $r$ "th rotor,

$$I_r \frac{d^2\theta_r}{dt^2} = -I_r n^2 \lambda_r \sin nt = (m_r - m_{r-1}) \sin nt,$$

or

$$-n^2 \lambda_r = (m_r - m_{r-1}) / I_r. \quad \dots \quad (1)$$

$$\text{Similarly, } -n^2 \lambda_{r+1} = (m_{r+1} - m_r) / I_{r+1}. \quad \dots \quad (2)$$

Subtracting, and multiplying by  $k_r$ ,

$$n^2 (\lambda_{r+1} - \lambda_r) k_r = n^2 m_r = (m_r - m_{r-1}) \frac{k_r}{I_r} - (m_{r+1} - m_r) \frac{k_r}{I_{r+1}}.$$

Writing  $n^2 = -u$ ,  $\frac{k_r}{I_r} = a_r$ ,  $\frac{k_r}{I_{r+1}} = b_r$ ,

$$m_{r+1} = \frac{[u + a_r + b_r]}{b_r} m_r - \frac{a_r}{b_r} m_{r-1}, \quad \dots \quad (3)$$

and if we now write

$$m_{r+1} = \frac{M_r}{\prod b_r} m_1, \quad \dots \quad (4)$$

where  $\prod b_r = b_1 b_2 b_3 \dots b_r$ ,

and  $M_r$  is a function of " $u$ " and of the elastic-inertia constants of shafts 1 to  $r$ ,

$$\frac{M_r}{\prod b_r} m_1 = \frac{(u + a_r + b_r)}{b_r} \frac{M_{r-1}}{\prod b_{r-1}} m_1 - \frac{a_r}{b_r} \frac{M_{r-2}}{\prod b_{r-2}} m_1.$$

Multiplying throughout by  $\frac{\prod b_r}{m_1}$ , we have

$$M_r = (u + a_r + b_r) M_{r-1} - a_r b_{r-1} M_{r-2}. \quad \dots \quad (5)$$

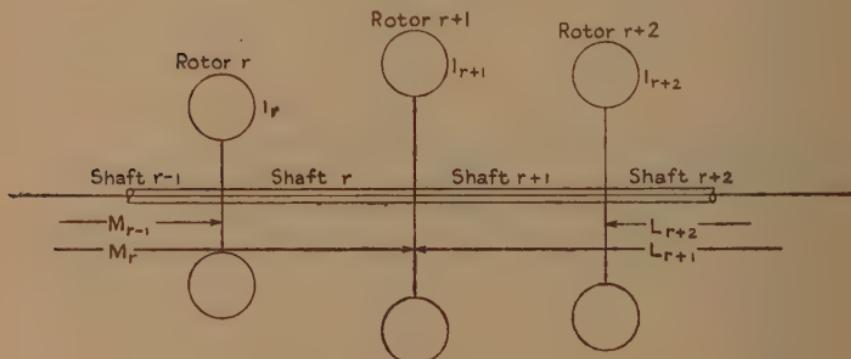
The function  $M_r$  is called the "torque function" of the part of the system which extends from rotor 1 to rotor  $(r+1)$  inclusive. When divided by  $I_{rb_r}$  it becomes the ratio between  $m_{r+1}$  and  $m_1$ .

Hence  $m_{N+1} = \frac{M_N}{I_{rb_N}} m_1 \dots \dots \dots \quad (6)$

But  $m_{N+1}$  is the torque exerted on the right-hand side of the extreme right-hand rotor, and this is, of course, zero for the state of free vibration.

Hence  $M_N = 0, \dots \dots \dots \quad (7)$

Fig. 1.



and this is the frequency equation of the system, giving  $u (= -n^2)$  in terms of the elastic-inertia constants.

The function  $M_N$  is of the  $N$ th degree in " $u$ ," and therefore the number of roots of the frequency equation is  $N$ , which is also the number of shafts in the system. The coefficient of  $u^N$  in  $M_N$  is unity.

It should be noted that  $M_0 = 1$ . This follows from the fact that  $M_2 = (u + a_2 + b_2)M_1 - a_2 b_1 M_0$ , whilst insertion of first  $r=1$  and then  $r=2$  in (3) shows that

$$M_2 = (u + a_2 + b_2)(u + a_1 + b_1) - a_2 b_1.$$

Fig. 1 shows three adjacent rotors in a system containing  $N$  shafts in all. The torque function applying to that part of the system which extends from rotor 1 to rotor  $(r+1)$  inclusive is  $M_r$ .

Now let the torque function for that part of the

system which extends from rotor N to rotor  $(r+1)$  inclusive be  $L_{r+1}$ .

$$\text{Then } m_{r+1} = \frac{L_{r+2}}{\prod a_{r+2} a_{r+3} \dots a_N} m_N. \quad \dots \quad (8)$$

$$\text{Similarly, } m_r = \frac{L_{r+1}}{\prod a_{r+1} a_{r+2} \dots a_N} m_N. \quad \dots \quad (9)$$

$$\text{Also } m_{r+1} = \frac{M_r}{\prod b_r} m_1, \quad \dots \quad (10)$$

$$\text{and } m_r = \frac{M_{r-1}}{\prod b_{r-1}} m_1. \quad \dots \quad (11)$$

By analogy with (5)

$$L_{r+1} = (u + a_{r+1} + b_{r+1}) L_{r+2} - b_{r+1} a_{r+2} L_{r+3}.$$

Equating the product of the quantities on the right-hand sides of (9) and (10) to that of the quantities on the right-hand sides of (8) and (11),

$$\frac{M_r L_{r+1}}{(\prod b_r)(\prod a_{r+1} a_{r+2} \dots a_N)} = \frac{M_{r-1} L_{r+2}}{(\prod b_{r-1})(\prod a_{r+2} a_{r+3} \dots a_N)},$$

$$\text{whence } M_r L_{r+1} - b_r a_{r+1} M_{r-1} L_{r+2} = 0. \quad \dots \quad (12)$$

This is the frequency equation for the whole system, and it is of the Nth degree in "u," since the degree of  $L_{r+1}$  is  $N-r$  and that of  $L_{r+2}$  is  $N-(r+1)$ . Moreover, the coefficient of  $u^N$  is unity, and consequently the left-hand side of (12) is identical with  $M_N$ .

From (2)

$$\begin{aligned} \lambda_{r+1} &= \frac{-1}{n^2 I_{r+1}} \left[ \frac{M_r}{\prod b_r} m_1 - \frac{M_{r-1}}{\prod b_{r-1}} m_1 \right] \\ &= -\frac{M_r - b_r M_{r-1}}{\prod b_r} \frac{m_1}{n^2 I_{r+1}}. \quad \dots \quad (13) \end{aligned}$$

Also, writing  $r=1$  in (1),  $m_1 = -n^2 I_1 \lambda_1$ , since  $m_0 = 0$ . Substituting this value of  $m_1$  in (13), and transposing,

$$\frac{\lambda_{r+1}}{\lambda_1} = \frac{M_r - b_r M_{r-1}}{\prod b_r} \frac{I_1}{I_{r+1}}. \quad \dots \quad (14)$$

Similarly, from consideration of the right-hand part of the system,

$$\begin{aligned} \lambda_{r+1} &= -\frac{a_{r+1} L_{r+2} - L_{r+1}}{\prod a_{r+1} \dots a_N} \frac{m_N}{n^2 I_{r+1}} \\ &= \frac{L_{r+1} - a_{r+1} L_{r+2}}{\prod a_{r+1} \dots a_N} \frac{M_{r-1}}{\prod b_{N-1}} \frac{m_1}{n^2 I_{r+1}}. \end{aligned}$$

Hence, writing  $m_1 = -n^2 I_1 \lambda_1$ ,

$$\frac{\lambda_{r+1}}{\lambda_1} = -\frac{L_{r+1} - a_{r+1} L_{r+2}}{\prod a_1 \dots a_N} \frac{M_{N-1}}{\prod b_{N-1}} \frac{I_1}{I_{r+1}} \dots . \quad (15)$$

Multiplying (14) and (15) together,

$$\begin{aligned} \left( \frac{\lambda_{r+1}}{\lambda_1} \right)^2 &= -(M_r - b_r M_{r-1})(L_{r+1} - a_{r+1} L_{r+2}) \\ &\quad \times \left( \frac{I_2 I_3 \dots I_{r+1}}{\prod k_1 \dots k_r} \right) \left( \frac{I_{r+1} \dots I_{N-1}}{\prod k_{r+1} \dots k_N} \right) \left( \frac{I_1}{I_{r+1}} \right)^2 \frac{M_{N-1}}{\prod b_{N-1}} \\ &= -\frac{I_1}{I_{r+1}} \frac{(M_r - b_r M_{r-1})(L_{r+1} - a_{r+1} L_{r+2})}{\prod a_1 \dots a_N} \frac{M_{N-1}}{\prod b_{N-1}}. \end{aligned} \quad (16)$$

$$\begin{aligned} \text{Now } (M_r - b_r M_{r-1})(L_{r+1} - a_{r+1} L_{r+2}) \\ &= M_r L_{r+1} - b_r M_{r-1} L_{r+1} - a_{r+1} L_{r+2} M_r + b_r a_{r+1} M_{r-1} L_{r+2} \\ &= M_r L_{r+1} - b_r a_{r+1} M_{r-1} L_{r+2} - b_r M_{r-1} (L_{r+1} - a_{r+1} L_{r+2}) \\ &\quad - a_{r+1} L_{r+2} (M_r - b_r M_{r-1}). \end{aligned}$$

But from (12)

$$M_r L_{r+1} - b_r a_{r+1} M_{r-1} L_{r+2} = 0.$$

Therefore

$$\begin{aligned} \left( \frac{\lambda_{r+1}}{\lambda_1} \right)^2 &= \frac{I_1}{I_{r+1}} \frac{M_{N-1}}{\prod a_N \prod b_{N-1}} \\ &\times [b_r M_{r-1} (L_{r+1} - a_{r+1} L_{r+2}) + a_{r+1} L_{r+2} (M_r - b_r M_{r-1})]. \end{aligned} \quad (17)$$

The ratio  $\lambda_{r+1}/\lambda_1$  is that of the ordinate of the normal elastic curve at rotor  $(r+1)$  to that at rotor 1.

### *Effect of varying $I_{r+1}$ .*

If  $I_{r+1}$  be changed the elastic-inertia constants  $b_r$  and  $a_{r+1}$  and the torque functions  $M_r$ ,  $L_{r+1}$ , and  $M_N$  are affected, whilst  $M_{r-1}$  and  $L_{r+2}$  are unaltered.

Since

$$b_r = k_r / I_{r+1},$$

$$\frac{\partial b_r}{\partial I_{r+1}} = -\frac{k_r}{I_{r+1}^2} = -\frac{b_r}{I_{r+1}}.$$

Similarly,

$$\frac{\partial a_{r+1}}{\partial I_{r+1}} = -\frac{a_{r+1}}{I_{r+1}}.$$

Now

$$M_r = (u + a_r + b_r) M_{r-1} - a_r b_{r-1} M_{r-2}.$$

Hence  $\frac{\partial M_r}{\partial I_{r+1}} = -\frac{b_r}{I_{r+1}} M_{r-1}.$

Similarly  $\frac{\partial L_{r+1}}{\partial I_{r+1}} = -\frac{a_{r+1}}{I_{r+1}} L_{r+2},$

Now  $M_N = M_r L_{r+1} - b_r a_{r+1} M_{r-1} L_{r+2}.$

Differentiating with respect to  $I_{r+1}$ ,

$$\begin{aligned}\frac{\partial M_N}{\partial I_{r+1}} &= M_r \left( -\frac{a_{r+1}}{I_{r+1}} \right) L_{r+2} + L_{r+1} \left( \frac{-b_r}{I_{r+1}} \right) M_{r-1} \\ &\quad - M_{r-1} L_{r+2} \left[ \frac{-2b_r a_{r+1}}{I_{r+1}} \right] \\ &= -\frac{1}{I_{r+1}} [b_r M_{r-1} (L_{r+1} - a_{r+1} L_{r+2}) \\ &\quad + a_{r+1} L_{r+2} (M_r - b_r M_{r-1})].\end{aligned}$$

Substituting for the quantity within the square bracket, its value as given by (17),

$$\frac{\partial M_N}{\partial I_{r+1}} = -\frac{\Pi a_N \Pi b_{N-1}}{I_1 M_{N-1}} \left( \frac{\lambda_{r+1}}{\lambda_1} \right)^2. \dots \quad (18)$$

Now, if  $I_{r+1}$  and "u" both vary,

$$\frac{dM_N}{d(u, I_{r+1})} = \frac{\partial M_N}{\partial u} + \frac{\partial M_N}{\partial I_{r+1}},$$

or

$$\Delta M_N = \frac{\partial M_N}{\partial u} \Delta u + \frac{\partial M_N}{\partial I_{r+1}} \Delta I_{r+1}.$$

If  $\Delta u$  is the change in "u" corresponding to the change in natural frequency produced by the alteration of  $I_{r+1}$  to  $I_{r+1} + \Delta I_{r+1}$ , the quantity  $\Delta M_N$  is zero, since  $M_N$  does not alter from its original value (zero). Hence

$$\begin{aligned}\Delta u &= - \left[ \frac{\partial M_N}{\partial I_{r+1}} / \frac{\partial M_N}{\partial u} \right] \Delta I_{r+1} \\ &= -\frac{\Pi a_N \Pi b_{N-1}}{I_1 M_{N-1} \left( \frac{\partial M_N}{\partial u} \right)} \left( \frac{\lambda_{r+1}}{\lambda_1} \right)^2 \Delta I_{r+1}. \dots \quad (19)\end{aligned}$$

Let the moment of inertia of every rotor be increased in the ratio  $(1+s)$  to 1, where "s" is small. Then all the elastic-inertia constants are reduced in the ratio 1

to  $(1+s)$  or approximately  $(1-s)$  to 1. Hence "u" changes to  $u(1-s)$ , and therefore  $\Delta u = -su$ .

$$\text{Also, } \Delta u = \frac{\Pi a_N \Pi b_{N-1}}{I_1 M_{N-1} \left( \frac{\partial M_N}{\partial u} \right)} \Sigma \left( \frac{\lambda}{\lambda_1} \right)^2 \Delta I, \quad \dots \quad (20)$$

and

$$\Delta I = (1+s)I - I = sI.$$

$$\text{Therefore } -su = -\frac{\Pi a_N \Pi b_{N-1}}{I_1 M_{N-1} \left( \frac{\partial M_N}{\partial u} \right)} s \Sigma \left( \frac{\lambda}{\lambda_1} \right)^2 I,$$

and so

$$\frac{\Pi a_N \Pi b_{N-1}}{I_1 M_{N-1} \left( \frac{\partial M_N}{\partial u} \right)} = \frac{-u}{\Sigma \left( \frac{\lambda}{\lambda_1} \right)^2 I}. \quad \dots \quad (21)$$

Therefore, substituting this value in (19),

$$\Delta u = \frac{-u}{\Sigma \left( \frac{\lambda}{\lambda_1} \right)^2 I} \left( \frac{\lambda_{r+1}}{\lambda_1} \right)^2 \Delta I_{r+1},$$

and

$$\frac{\Delta u}{u} = \frac{-\lambda_{r+1}^2 \Delta I_{r+1}}{\Sigma \lambda^2 I}. \quad \dots \quad (22)$$

If the ordinates of the normal elastic curve are known this equation affords a very convenient method of calculating the approximate change in natural frequency produced by a small change in the moment of inertia of any rotor in the system. The values of  $\lambda$  and  $\lambda_{r+1}$  are taken from the normal elastic curve associated with the particular vibration-form under consideration.

### *Effect of varying $k_{r+1}$ .*

If  $k_{r+1}$  be changed the elastic-inertia constants  $a_{r+1}$  and  $b_{r+1}$  are changed, and with them the expression for  $L_{r+1}$ .

Since

$$a_{r+1} = k_{r+1}/I_{r+1}, \quad \frac{\partial a_{r+1}}{\partial k_{r+1}} = \frac{1}{I_{r+1}} = \frac{a_{r+1}}{k_{r+1}}.$$

Similarly,

$$\frac{\partial b_{r+1}}{\partial k_{r+1}} = \frac{b_{r+1}}{k_{r+1}}.$$

Now,  $L_{r+1} = (u + a_{r+1} + b_{r+1})L_{r+2} - b_{r+1}a_{r+2}L_{r+3}$ .

Therefore

$$\begin{aligned}\frac{\partial L_{r+1}}{\partial k_{r+1}} &= \frac{(a_{r+1} + b_{r+1})}{k_{r+1}} L_{r+2} - \frac{b_{r+1} a_{r+2}}{k_{r+1}} L_{r+3} \\ &= \frac{1}{k_{r+1}} [L_{r+1} - u L_{r+2}].\end{aligned}$$

Now  $M_N = M_r L_{r+1} - b_r a_{r+1} M_{r-1} L_{r+2}$ .

Differentiating with respect to  $k_{r+1}$ ,

$$\begin{aligned}\frac{\partial M_N}{\partial k_{r+1}} &= \frac{M_r}{k_{r+1}} [L_{r+1} - u L_{r+2}] - \frac{b_r a_{r+1}}{k_{r+1}} M_{r-1} L_{r+2} \\ &= \frac{1}{k_{r+1}} [-u M_r L_{r+2} + M_r L_{r+1} - b_r a_{r+1} M_{r-1} L_{r+2}],\end{aligned}$$

and since  $M_r L_{r+1} - b_r a_{r+1} M_{r-1} L_{r+2} = M_N = 0$ ,

$$\frac{\partial M_N}{\partial k_{r+1}} = -\frac{u M_r L_{r+2}}{k_{r+1}}. \quad \dots \quad (23)$$

Now if  $\Delta u$  is the change in "u" corresponding to a change  $\Delta k_{r+1}$  in  $k_{r+1}$ , we have, by analogy with the first part of (19),

$$\begin{aligned}\Delta u &= - \left[ \frac{\partial M_N}{\partial k_{r+1}} \middle| \frac{\partial M_N}{\partial u} \right] \Delta k_{r+1} \\ &= \left[ \frac{u M_r L_{r+2}}{k_{r+1}} \middle| \frac{\partial M_N}{\partial u} \right] \Delta k_{r+1}.\end{aligned}$$

Hence  $\frac{\Delta u}{u} = \left[ \frac{M_r L_{r+2}}{\left( \frac{\partial M_N}{\partial u} \right)} \right] \frac{\Delta k_{r+1}}{k_{r+1}} \dots \quad (24)$

The approximate change in natural frequency produced by a change in stiffness of any shaft is conveniently calculated from (24) if the torque functions ( $M_r$  and  $L_{r+2}$ ) are known for the two portions of the system that are joined by the shaft in question.

Now  $m_{r+1} = \frac{M_r}{I I b_r} m_1$ .

Also  $m_{r+1} = \frac{L_{r+2}}{I I a_{r+2} \dots a_N} m_N$   
 $= \frac{L_{r+2}}{I I a_{r+2} \dots a_N} \frac{M_{N-1}}{I I b_{N-1}} m_1$ .

Multiplying these together,

$$(m_{r+1})^2 = \frac{M_r L_{r+2}}{(\Pi b_r) \Pi a_{r+2} \dots a_N} \frac{M_{N-1}}{\Pi b_{N-1}} m_1^2$$

$$(\Pi b_r) \Pi a_{r+2} \dots a_N = \binom{k_1 k_2 \dots k_r}{I_2 I_3 \dots I_{r+1}} \frac{k_{r+2} k_{r+3} \dots k_N}{I_{r+2} I_{r+3} \dots I_N}$$

$$= \frac{I_1}{k_{r+1}} \frac{\Pi k_1 k_2 \dots k_N}{\Pi I_1 I_2 \dots I_N} = \frac{I_1}{k_{r+1}} \Pi a_N.$$

Hence  $M_r L_{r+2} = \left( \frac{m_{r+1}}{m_1} \right)^2 \frac{I_1}{k_{r+1}} (\Pi a_N) \frac{\Pi b_{N-1}}{M_{N-1}}.$

From (21)

$$\frac{(\Pi a_N) \Pi b_{N-1}}{M_{N-1}} = \frac{-u I_1}{\Sigma \binom{\lambda}{\lambda_1}^2 I} \left( \frac{\partial M_N}{\partial u} \right),$$

and from (24)

$$\frac{\Delta u}{u} = \frac{n^2 I_1}{k_{r+1}} \left( \frac{m_{r+1}}{m_1} \right)^2 \frac{1}{\Sigma \binom{\lambda}{\lambda_1}^2 I} \frac{\Delta k_{r+1}}{k_{r+1}}. \dots \quad (25)$$

Substituting

$$\frac{n^2 I_1}{m_1^2} = \frac{-1}{m_1 \lambda_1} = \frac{1}{k_1 \lambda_1 (\lambda_1 - \lambda_2)}$$

and  $\frac{m_{r+1}}{k_{r+1}} = \lambda_{r+2} - \lambda_{r+1},$

equation (25) becomes

$$\frac{\Delta u}{u} = \frac{1}{\Sigma \binom{\lambda}{\lambda_1}^2 I} \frac{(\lambda_{r+1} - \lambda_{r+2})^2}{\lambda_1 (\lambda_2 - \lambda_1)} \frac{\Delta k_{r+1}}{k_1}. \dots \quad (26)$$

This equation is a convenient alternative to (24) for use when the torque functions have not been determined but the form of the normal elastic curve is known.

### Numerical Example.

To illustrate the application of these methods the system shown in fig. 2 may be discussed.

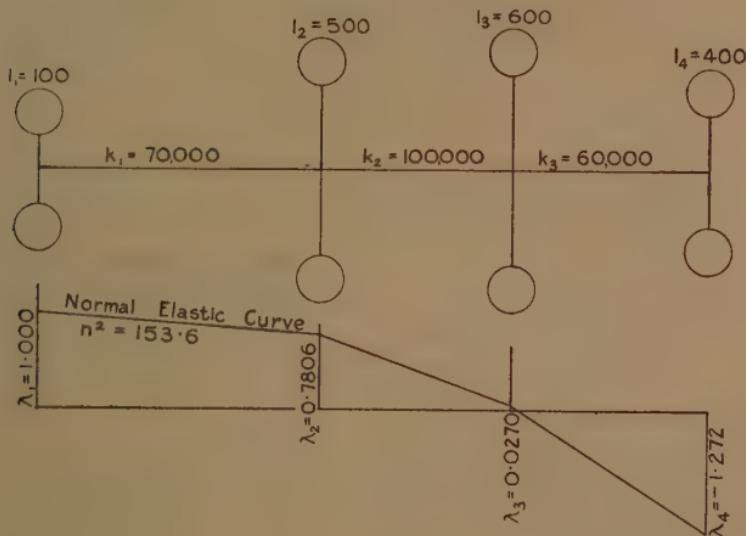
The elastic-inertia constants are :

$$a_1 = \frac{70000}{100} = 700.$$

$$b_1 = \frac{70000}{500} = 140. \quad \text{Hence } a_1 + b_1 = 840.$$

$$a_2 = \frac{100000}{500} = 200. \quad \text{Hence } a_2 b_1 = 28000.$$

Fig. 2.



$$b_2 = \frac{100000}{600} = 166.7. \quad \text{Hence } a_2 + b_2 = 366.7.$$

$$a_3 = \frac{60000}{600} = 100. \quad \text{Hence } a_3 b_2 = 16667.$$

$$b_3 = \frac{60000}{400} = 150. \quad \text{Hence } a_3 + b_3 = 250.$$

It is convenient for numerical purposes to divide each of these constants by 100, when the argument "u" of the frequency equation is  $\frac{-n^2}{100}$  instead of  $-n^2$ .

Then

$$\begin{array}{ll} a_1 + b_1 = 8.4 & a_2 b_1 = 2.8 \\ a_2 + b_2 = 3.667 & a_3 b_2 = 1.667 \\ a_3 + b_3 = 2.5 & \end{array}$$

The determination of the coefficients of the powers of "u" in the various torque functions proceeds thus :—

### Coefficients of Powers of "u."

	$u^0.$	$u^1.$	$u^2.$	$u^3.$
$M_0 \dots\dots\dots$	1			
$M_1 = u + a_1 + b_1 \dots$	8.4	1		
$(a_2 + b_2)M_1 \dots\dots\dots$	30.8	3.667		
$uM_1 \dots\dots\dots$	—	8.4	1	
$(u + a_2 + b_2)M_1 \dots\dots\dots$	30.8	12.067	1	
$-a_2 b_1 M_0 \dots\dots\dots$	-2.8			
<hr/>				
$M_2 \dots\dots\dots$	28.0	12.067	1	
$(a_3 + b_3)M_2 \dots\dots\dots$	70.0	30.167	2.5	
$uM_2 \dots\dots\dots$	—	28.0	12.067	1
$(u + a_3 + b_3)M_2 \dots\dots\dots$	70.0	58.167	14.567	/1
$-a_3 b_2 M_1 \dots\dots\dots$	-14.0	-1.667		
<hr/>				
$M_3 \dots\dots\dots$	56.0	56.5	14.567	1

Thus the torque functions are determined in order from left to right. A similar process, working through the system from right to left, gives the torque functions  $L_3$ ,  $L_2$ ,  $L_1$ , and a useful check on the working is provided by the fact that  $L_1$  must be identical with  $M_3$ . It is found that

$$L_4 = 1, L_3 = 2.5 + u, L_2 = 7.5 + 6.167u + u^2,$$

$$L_1 = 56.0 + 56.5u + 14.567u^2 + u^3.$$

Equating  $M_3$  (or  $L_1$ ) to zero, and solving the equation by Horner's Method, the lowest root is found to be -1.536, and therefore  $n^2 = 153.6$ , whence the lowest

natural frequency is  $\frac{1}{2\pi}\sqrt{153.6}$ , the unit depending on those of torsional stiffness and of moment of inertia.

The relative amplitudes of vibration at the different rotors may be found by use of (17), but a shorter method, which also provides another check on the value of  $n^2$ , is given below. It is based on the relation

$$\lambda_r - \lambda_{r+1} = -\frac{m_r}{k_r} = \frac{1}{k_r} [n^2 I_1 \lambda_1 + n^2 I_2 \lambda_2 + \dots n^2 I_r \lambda_r],$$

which gives the difference between the amplitudes of angular displacement at adjacent rotors. On the basis of an arbitrary value assigned to  $\lambda_1$  the values of  $\lambda$  at the other rotors are obtained in turn thus :—

$$n^2 = 153.6.$$

I.	$In^2/10^4$ .	$\lambda_r$	$In^2\lambda/10^4$ .	$\Sigma In^2\lambda/10^4$ .	$10^4/k_r$	$\lambda_r - \lambda_{r+1}$ .
100	1.536	1.000	1.536	1.536	0.1429	0.2194
500	7.680	0.7806	6.000	7.536	0.1000	0.7536
600	9.108	0.0270	0.244	7.780	0.1667	1.297
400	6.144	-1.272	-7.800	-0.02		

In the first line  $\lambda$  is given the arbitrary value unity. The value of  $\lambda_r - \lambda_{r+1}$  obtained in each line is subtracted from the value of  $\lambda$  in that line to give the value of  $\lambda$  for the succeeding line. The factor  $10^4$  is introduced to avoid inconveniently large numbers.

Since the total external torque applied to the system is zero, the sum of the torques on all the rotors is zero. Hence  $\Sigma In^2\lambda$  should be zero when all the rotors are included if the adopted value of "n" corresponds to a natural frequency of the system. Allowing for arithmetical inaccuracies the figure -0.02 on line 4, column 5, confirms this, and therefore proves that  $n^2=153.6$  corresponds to a natural frequency of the system. The circumstance that there is only one change of sign in column 3 shows that there is only one node, and therefore that  $n^2=153.6$  gives the lowest natural frequency.

Now let it be desired to determine the approximate

effect on the lowest natural frequency of the following changes in the elements of the system:

- (a)  $k_2$  increased from 100,000 to 120,000.
- (b)  $I_2$  reduced from 500 to 440.
- (c)  $I_4$  reduced from 400 to 350.

From the table above

$$I_1 \lambda_1^2 = 100.$$

$$I_2 \lambda_2^2 = 305.$$

$$I_3 \lambda_3^2 = 0.44.$$

$$I_4 \lambda_4^2 = 646.$$

$$\overline{\Sigma I \lambda^2} = 1051. \quad \Sigma \left( \frac{\lambda}{\lambda_1} \right)^2 \frac{I}{I_1} = 10.51.$$

(a) Inserting in (26) the known values of the various quantities, including  $r=1$ ,

$$\frac{\Delta u}{u} = \frac{1}{10.51} \frac{(0.7536)^2}{1 \times 0.2194} \frac{20000}{70000} = 0.0703,$$

or, making use of (24),

$$M_1 = 8.4 + u = 8.4 - 1.536 = 6.864.$$

$$L_3 = 2.5 + u = 2.5 - 1.536 = 0.964.$$

$$\frac{\partial M_N}{\partial u} = 56.5 + 29.133u + 3u^2 = 18.85 \text{ (when } u = -1.536).$$

Hence,

$$\frac{\Delta u}{u} = \frac{6.864 \times 0.964}{18.85} \times \frac{20000}{100000} = 0.0703.$$

(b) Using (22),

$$\Delta I_{r+1} = -60,$$

$$\frac{\Delta u}{u} = - \frac{(0.7806)^2 \times (-60)}{1051} = 0.0348.$$

(c) Using (22),

$$\Delta I_{r+1} = -50,$$

$$\frac{\Delta u}{u} = - \frac{(-1.272)^2 \times (-50)}{1051} = 0.077.$$

Hence, total change in "u"

$$\begin{aligned} &= -1.536 [0.0703 + 0.0348 + 0.077] \\ &= -0.280, \end{aligned}$$

and therefore

$$u = -1.536 - 0.280 = -1.816 \text{ or } n^2 = 181.6.$$

A direct calculation of the frequency of the new system gives  $n^2 = 183.0$ , so that the error in the approximate solution is less than 1 per cent.

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XCI. *A Generalization of the Lorentz Transformation.*

By K. V. SASTRY, M.Sc., Research Scholar, Benares Hindu University, India \*.

A GENERALIZATION of the Lorentz transformation has been given by Mr. F. Tavani † in two recent papers in the 'Philosophical Magazine,' where the relative motion of two observers is considered to be non-uniform and curvilinear and average velocities along the axes appear as parameters, probably, varying slowly with time. It seems more reasonable to suppose that in a generalization of the transformation that is to hold good at a particular epoch it is the velocity vector at that epoch that should appear rather than the average velocity. The formulae of Tavani's papers fail when the relative motion is a periodic motion, so that the average velocity after a finite interval of time is zero. We give here an alternative and, perhaps, a more satisfactory generalization of the Lorentz transformation.

Let  $k$  and  $k'$  be two observers, one always at the origin of a frame  $0-xyzt$  and the other always at the origin of the frame  $0'-x'y'z'i'$ . Let the corresponding space-axes always remain parallel, and let the two observers be together at the epoch  $t=0$ .  $k'$  moves relative to  $k$  along a curve, not necessarily with a uniform velocity, so that at time  $t$   $k'$  is at  $(x_1, y_1, z_1)$  and has a velocity  $v$  with direction cosines  $\cos \theta_1, \cos \theta_2, \cos \theta_3$ . If the tangent to

\* Communicated by V. V. Narlikar.

† Phil. Mag. ser. 7, xvii. no. 117, p. 187; xix. no. 129, p. 1055.

the orbit of  $k'$  at  $(x_1, y_1, z_1)$  meets the  $xy$  plane at  $(x_0, y_0, 0)$  we have three parameters,  $t_1, t_2, t_3$ , each of the dimension of time, defined by

$$x_1 = x_0 + vt_1 \cos \theta_1, \quad \dots \quad \dots \quad \dots \quad (1)$$

$$y_1 = y_0 + vt_2 \cos \theta_2, \quad \dots \quad \dots \quad \dots \quad (2)$$

$$z_1 = vt_3 \cos \theta_3, \quad \dots \quad \dots \quad \dots \quad \dots \quad (3)$$

We suggest now the following formulæ for a generalization of the Lorentz transformation :—

$$x'\beta_1 = x - x_0 - vt_1 \cos \theta_1, \quad x\beta_1 = x' + x_0 + vt_1' \cos \theta_1, \quad (4)$$

$$y'\beta_2 = y - y_0 - vt_2 \cos \theta_2, \quad y\beta_2 = y' + y_0 + vt_2' \cos \theta_2, \quad (5)$$

$$z'\beta_3 = z - z_0 - vt_3 \cos \theta_3, \quad z\beta_3 = z' + z_0 + vt_3' \cos \theta_3, \quad (6)$$

where

$$\beta_1 = (1 - v^2 \cos^2 \theta_1 c^2)^{\frac{1}{2}}, \quad \beta_2 = (1 - v^2 \cos^2 \theta_2 c^2)^{\frac{1}{2}},$$

$$\beta_3 = (1 - v^2 \cos^2 \theta_3 c^2)^{\frac{1}{2}}.$$

$t_1', t_2', t_3'$  are the analogues of  $t_1, t_2, t_3$ ; their transformation formulæ may be obtained from (4), (5), and (6). Thus the transformation connecting  $t_1$  and  $t_1'$  is

$$\beta_1 vt_1' \cos \theta_1 = x_0(1 - \beta_1) + vt_1 \cos \theta_1 - x(1 - \beta_1^2). \quad \dots \quad (7)$$

Defining the time coordinates  $t$  and  $t'$  by the relations

$$t = \int [(dt_1)^2 + (dt_2)^2 + (dt_3)^2]^{\frac{1}{2}}, \quad t' = \int [(dt_1')^2 + (dt_2')^2 + (dt_3')^2]^{\frac{1}{2}}, \quad \dots \quad \dots \quad (8)$$

it may be easily verified that

$$dx'^2 + dy'^2 + dz'^2 - c^2 dt'^2 = dx^2 + dy^2 + dz^2 - c^2 dt^2. \quad (9)$$

The relation (9) holds good so long as the variation with time of  $x_0, y_0, v, \cos \theta_1, \cos \theta_2$ , and  $\cos \theta_3$  is negligible—that is, so long as the velocity vector remains practically constant. A variation of the velocity vector at any particular epoch brings in the complications of a field of force in the transformation formulæ for that epoch. The formulæ (4), (5), (6), and (8) satisfy (9), and thus give a generalized Lorentz transformation valid for some interval  $t_1 < t < t_2$  during which the velocity vector is practically constant. It may be noted that while we assume the existence of such an interval about  $t$ , no matter how small, for the validity of the transformation we make no assumption whatsoever about the nature of the motion for  $0 < t < t_1$ . It is in this, if anywhere, the merit of this generalization may be found.

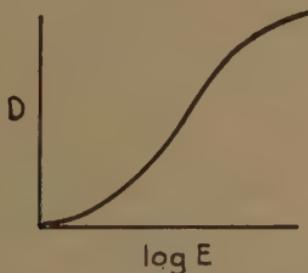
XCII. *The Characteristic Curve of the Photographic Plate.*

By R. A. HOUSTOUN, D.Sc., F.Inst.P., Lecturer on Physical Optics in the University of Glasgow \*.

THE purpose of this note is to suggest an equation for the characteristic curve of the photographic plate.

The speed and contrast of a photographic plate are specified by its characteristic curve. An example of such a curve is shown in fig. 1; it is obtained by giving the material a series of exposures, and then, after development, measuring the optical density  $D$  of the silver deposit and plotting it against the logarithm of the exposure,  $\log E$ . The optical density is defined as the logarithm

Fig. 1.



to base 10 of the ratio of  $I_0$ , the intensity of the light incident on the negative, to  $I$ , the intensity of the light transmitted. The exposures may be for the same intensity of light and different times or for the same time and different intensities. In each case  $E$  is proportional to the quantity of light falling on the plate. The curve shows that the density increases with logarithm of exposure, at first slowly, then more rapidly, after which it approaches a constant value.

The light sensitive emulsion consists of silver bromide particles embedded in a layer of gelatine. The size of the particles varies with the speed of the emulsion; in the fastest emulsions they may measure as much as one-hundredth of a millimetre across. If the plate is exposed to light and fully developed it is found that after development some of the particles are completely reduced to

\* Communicated by the Author.

metallic silver while others are quite unaffected. A big density means a large percentage of grains changed. If development is stopped before it is fully completed the particles affected are only partially reduced to silver. At some time during its exposure each particle which is developable, undergoes a sudden change in its character.

The question arises as to why some particles are taken and others left. Two answers have been put forward—the “nuclear theory,” according to which the particles have different thresholds, each becoming developable when the exposure reaches its threshold, and the “light dart theory,” according to which light consists of bundles or darts of energy, the grain becoming developable if it is hit by one or more of these darts.

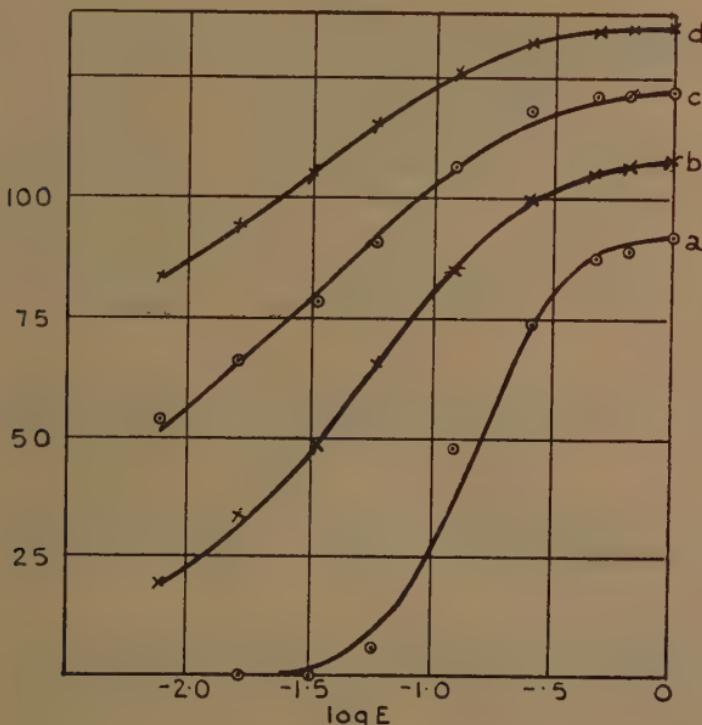
The nuclear theory has been advocated in two interesting papers by F. C. Toy<sup>(1)</sup>. It is generally believed that the action of light is to form in or near the surface of the grain certain “centres” or “points of infection” which act as starting points for the developer. Toy takes the view, which is supported by chemical evidence, that at these centres there are invisibly small specks of silver sulphide, and that it is on these specks that the light acts. These specks are distributed amongst the grains haphazard according to the laws of chance. Whenever the exposure reaches the threshold or sensitivity of the speck with the lowest threshold the whole grain becomes developable. Since the nuclei are all formed in the same emulsion most of them will have a sensitivity near the average value for the whole, and there will be a few which are very sensitive and a few which are very insensitive. The curve giving the distribution of the sensitivities of the nuclei in terms of  $E$  will be a probability curve, but its exact form is immaterial. There are two reasons why large grains are more sensitive than small grains; firstly, there are more nuclei present in the larger grains, secondly, the average sensitivity of the nuclei increases with the size of the grain.

The light dart theory was formulated and developed by L. Silberstein<sup>(2)</sup>, and finally abandoned by its author<sup>(3)</sup>, after an exhaustive investigation of its possibilities, as being inconsistent with the facts. He then proceeded to put Toy’s theory in a more definite mathematical form. Toy had left the distribution curve of the sensitivities of his centres indefinite. Silberstein assumes that the most

sensitive nuclei of each grain form an ordinary Gaussian distribution curve when expressed in terms of  $E$ . He next makes the additional assumption that the nuclei swell under the action of light, and only when they attain a certain diameter do they become active. This introduces a third constant into the formula, which then gives a satisfactory representation of the results.

Both F. C. Toy and L. Silberstein test their theories by means of characteristic curves of a special nature. These

Fig. 2.



were obtained by counting the numbers of grains made developable at different exposures by means of the microscope. In this way it is possible to classify the grains according to size and get separate results for different sizes from one plate. I have represented all their data in figs. 2, 3, 4, and 5.

The observations shown in fig. 2 are taken from Toy's first paper and those shown in fig. 3 from his second paper.  $a$ ,  $b$ ,  $c$ , and  $d$  (fig. 2) are for grains of cross-sectional area

$0.98 \mu^2$ ,  $1.75 \mu^2$ ,  $2.73 \mu^2$ , and  $3.93 \mu^2$  respectively. In order to have a clear diagram *b*, *c*, and *d* are plotted one

Fig. 3.

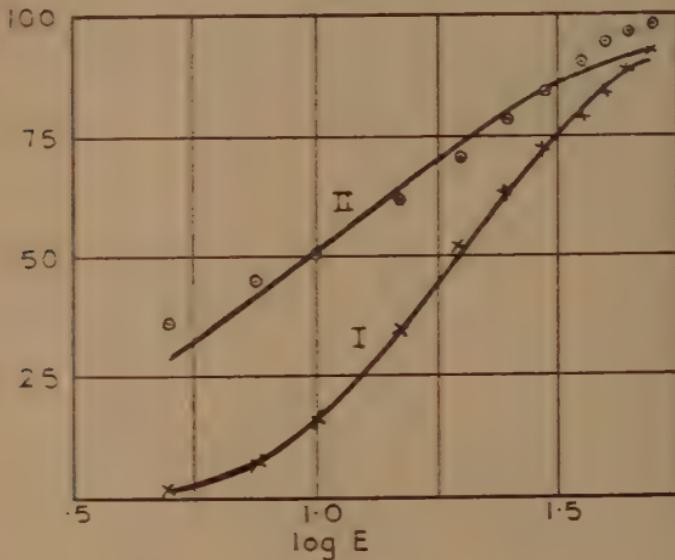
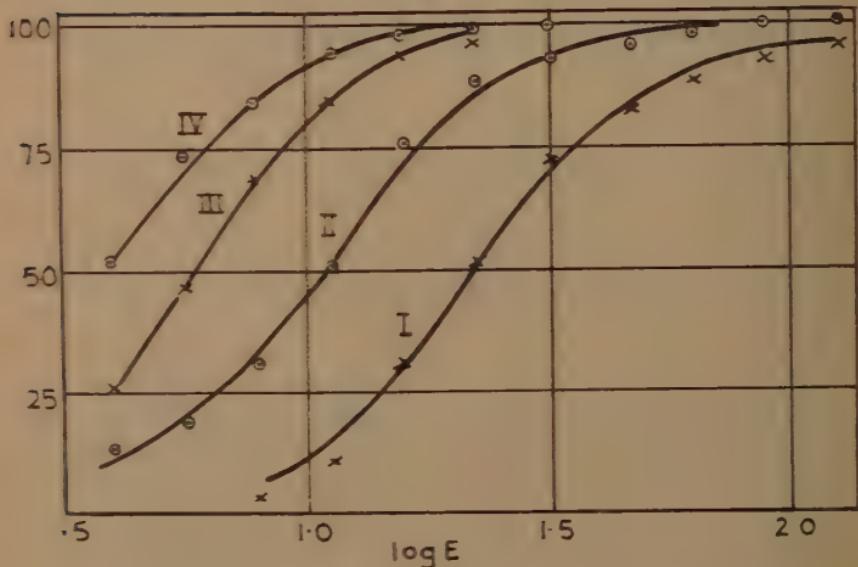


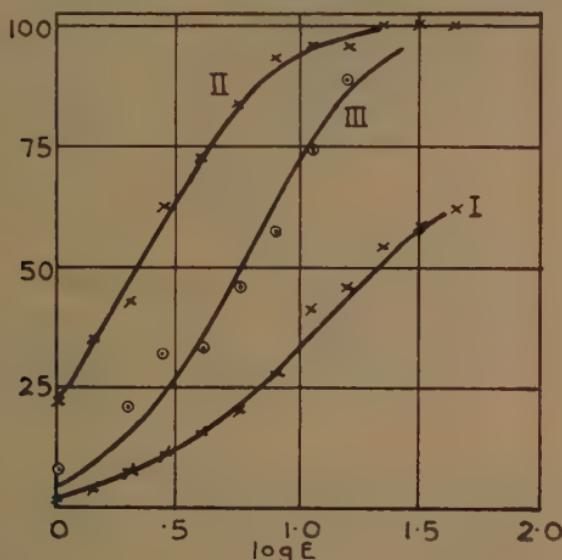
Fig. 4.



half square, one square, and one and a half squares too high. I and II (fig. 3) are for an Ilford process emulsion,

the diameters of the grains being  $0.60 \mu$  and  $0.75 \mu$  respectively. The observations shown in figs. 4 and 5 are from Silberstein's last paper. Fig. 4 gives data of Sheppard, Trivelli, and Loveland on a slow process emulsion, the size of the grains being  $0.115$ ,  $0.3$ ,  $0.5$ , and  $0.7 \mu^2$ ; fig. 5, I and II, gives data obtained by Trivelli and Loveland on Eastman 40 emulsion, and fig. 5, III, data obtained by Trivelli and Loveland on a pure bromide emulsion. The abscissæ give  $\log E$  on different arbitrary scales and the ordinates the percentage of grains rendered developable.

Fig. 5.



It seems to me, from an inspection of the diagram, that all we are entitled to assume from them is that the thresholds of the most sensitive nuclei in each grain form a Gaussian distribution in terms of  $\log E$ , and that Silberstein's assumptions are unnecessarily complicated. The smooth curves have been fitted to the data on this basis by trial and error—that is, the ordinate of the curve is given by

$$\int_{-\infty}^{\log E} e^{-(\log E/E_0)^2/2\sigma^2} d(\log E),$$

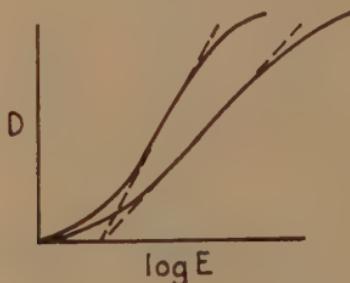
a two-constant formula, in place of Silberstein's three-constant formula. In one case (fig. 5, III) Silberstein's

formula gives better results, but Silberstein does not attempt to represent two of the curves (fig. 3, II, and fig. 5, I), and, generally speaking, the simpler formula is quite as satisfactory as the more elaborate one.

Since the position and scatter of the Gaussian distribution vary with the size of the grains it seems natural to explain any want of agreement by lack of homogeneity of the grains. Thus, if the distribution is not symmetrical we can assume there is a smaller distribution on one side of it.

I have found in connexion with vision that the magnitude of the sensation of light is given as a function of the intensity by an expression of the same form as the above<sup>(4)</sup>, and have interpreted it by the assumption that the percipient elements in the retina have different

Fig. 6.



thresholds. But there is an important difference between the retina and the photographic plate. In the retina the percipient elements are being continuously reconstituted.

It is found that when plates having sensitometric exposures on them are developed for different lengths of time, the straight line portions of the characteristic curves usually intersect approximately at the same point on the  $\log E$  axis, the inertia point (*cf.* fig. 6). The ordinates of the most important part of the curve therefore always increase in the same ratio. Thus the grains seem to be developed at the same rate. When the area of one is half covered the areas of all are half covered; it is not a case of the smaller grains finishing first.

Of course the density produced does not depend only on  $E$ , but also on the rate of illumination. This is referred to as the breakdown of the reciprocity law.

There is a most favourable rate for which the density is a maximum for a given quantity of energy. The most plausible way of explaining this is to make a distinction between the energy received by the centre and the energy effective, denoting the latter quantity by the symbol E. Some of the first energy received may be required to put the centre into a state for accumulating energy, and some of the energy received may be radiated before the grain is made developable. The breakdown of the reciprocity law, it may be noted, has recently been explained on the light dart theory by Silberstein and Webb<sup>(5)</sup>.

In the experimental work on the breakdown of the reciprocity law the exposures in many cases take days or even weeks. It is very difficult in this case to imagine any mechanism that would account for the slow accumulation of energy, the only one known to the author being Larmor's escapement mechanism<sup>(6)</sup>, which has never been favourably received.

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- (1) Phil. Mag. xliv. p. 352 (1922); xlv. p. 715 (1923).
- (2) Phil. Mag. xliv. pp. 257, 956 (1922); xlv. p. 1062 (1923).
- (3) Phil. Mag. v. p. 464 (1928).
- (4) 'Vision and Colour Vision.' London, 1932.
- (5) Phil. Mag. xviii. p. 1 (1934).
- (6) Phil. Mag. xlii. p. 592 (1921).

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### *XCIII. Magnetic Susceptibilities of Organic Substances in Different Physical States. By AKSHAYANANDA BOSE, M.Sc., Research Scholar, Indian Association for the Cultivation of Science, Calcutta \*.*

#### *1. Introduction.*

THE extensive magnetic measurements of Pascal on organic substances are very well known. The measurements were in general made on the substances as they actually occur at room-temperature, either as solids or liquids. On the basis of these measurements he deduced his well-known additive law and calculated the characteristic atomic and structural constants.

\* Communicated by Prof. K. S. Krishnan, D.Sc.

The remarkable success of the additive law in predicting the molecular susceptibilities of his organic compounds, whether they were solids or liquids, suggests that the molecular susceptibility is independent of the physical state of the substance, at any rate to a first approximation.

The well-known researches of Oxley \* on the change of susceptibilities of several organic substances on melting, point, however, to a large dependence of the susceptibility on the physical state. For example, with nitrobenzene the increase of susceptibility on melting is as much as 13 per cent., and in other aromatic compounds a change of 5 to 6 per cent. is very common. More recently, Cabrera and Fahlenbrach † report an even higher change, *e. g.*, 23 per cent. for nitrobenzene.

On the other hand, some measurements by Krishnan, Guha, and Banerjee ‡ on the susceptibilities of single crystals of naphthalene show that the mean of the three principal susceptibilities of the crystal is practically the same as the susceptibility of the molten substance.

In view of this conflicting evidence regarding the dependence of diamagnetic susceptibilities on the physical state of the substance, the present writer has made some detailed measurements on a number of organic substances (for which single crystal measurements are available from the recent work of Krishnan and Banerjee §) in the molten state, and generally also in a state of solution in suitable solvents. An account of these measurements is given in this paper.

## 2. Measurements with Molten Substances.

Since the measurements with solutions were made at room-temperature, while those with molten substances were made at high temperatures, it was found convenient to use different methods for the two sets of measurements.

For the molten substances the modified Gouy method described in a recent paper || in connexion with measurements on aqueous solutions of manganous and ferric salts was adopted. The liquid was contained in a long

\* Phil. Trans. cccxv. p. 109 (1914), cccxv. p. 79 (1915), and cccxx. p. 247 (1926).

† Zeits. f. Phys. lxxxv. p. 568 (1933).

‡ Phil. Trans. A, cccccxi. p. 235 (1933).

§ Phil. Trans. A, cccxxiv. p. 265 (1935), and cccxi. p. 235 (1933).

|| Proc. Ind. Acad. Sci. A, i. p. 605 (1934).

test-tube of pyrex glass, of uniform bore, and was suspended from one arm of a sensitive balance; the lower end of the liquid column was in the centre of a strong homogeneous field, while the upper level of the liquid was considerably outside the field. The force acting on the liquid column, due to the magnetic field, was compared with that on specially purified water, under the same conditions. The liquids could be heated to any desired temperature by passing hot water from a thermostat, or steam, through a double-walled glass jacket tube, surrounding the suspended system completely.

Since the forces were much smaller in the present measurements than with paramagnetic solutions, the diameter of the jacket tube had to be reduced to a minimum (without, of course, reducing the diameter of the suspended test-tube), so as to enable the pole pieces to be brought much closer and thus obtain a much larger field. In the above arrangement, with a current of 10 amperes through the magnetizing coils, the field was about 10,000 gauss, corresponding to a force of about 0.05 gm. on the water column.

The choice of the substances for measurement was restricted to those that melt below 100° C., so that they could be melted and kept at a suitable temperature by the circulation of water from the thermostat.

A preliminary weighing of the empty test-tube in the magnetic field, at different temperatures, supplied the necessary correction for the containing vessel.

The variation of the cross-section of the test-tube, and therefore of the liquid column, due to the thermal expansion of the glass (which was pyrex), was quite negligible.

The densities of the molten substances were determined by using an ordinary long-necked pyknometer.

Let  $k'_i$  be the volume susceptibility of the molten substance at the temperature of measurement,  $t$ , and  $k'_w$  that of water at room-temperature,  $r$ , and let  $k'_a$  and  $k'_u$  be the volume susceptibilities of air at these two temperatures. Further, let  $W'_i$  be the force due to the magnetic field acting on the liquid at temperature  $t$ , and  $W'_w$  that acting on water at room-temperature under the same conditions, both  $W'_i$  and  $W'_w$  having been corrected for the force on the empty test-tube containing the liquids.

Plainly, then,

$$k_t^t = \frac{tW(k_w^r - k_n^r)}{W_w^r} + k_a^t. \quad . . . . . \quad (1)$$

All the quantities on the right-hand side are known;  $k_a^t$  and  $k_r^t$  are obtained from the formula

$$k_a = \frac{p}{760} \cdot \left( \frac{293}{T} \right)^2 \times 0.0294 \times 10^{-6}, \quad . . . \quad (2)$$

where  $T$  and  $p$  are the temperature in degrees Kelvin and pressure in mm. of mercury of the air in the particular measurement ( $0.0294 \times 10^{-6}$  is the volume susceptibility of air at  $293^\circ K$  and 760 mm. pressure).  $k_t^t$  is therefore easily calculated.

### 3. Measurements with Solutions.

The method of measurement used for the solutions was the well-known Quincke method. Here the liquid is contained in a U-tube, one arm of which is very narrow compared with the other. The liquid level in the narrow limb is at the centre of a strong homogeneous magnetic field, while the wider limb is entirely outside the field. When the field is put on, the liquid level in the narrow limb is depressed or raised according as the liquid is dia- or paramagnetic. In our experiment the movement of the liquid meniscus was compared with that of water kept in a similar U-tube placed alongside the former tube by photographing the movements of the two menisci simultaneously under high magnification. This method has the advantage that the photograph could be taken in a short time, and it was therefore not necessary to take any special precaution for maintaining the field constant. The mass susceptibility of the liquid is proportional to the fall of the liquid column, except for a small correction term due to the presence of a mixture of air and the vapour of the liquid above the liquid column.

Let  $h_s$  be the depression in the level of the solution due to the action of the field,  $\chi_s$  the mass susceptibility,  $\rho_s$  the density and  $f_s$  the vapour pressure of the solution. Let the corresponding quantities for water be  $h_w$ ,  $\chi_w$ ,  $\rho_w$  and  $f_w$ . We then have

$$\frac{h_s}{h_w} = \frac{\chi_s - \frac{760-f_s}{760 \cdot \rho_s} \times 0.029 \times 10^{-6}}{\chi_w - \frac{760-f_w}{760 \cdot \rho_w} \times 0.029 \times 10^{-6}} \quad \dots \quad (3)$$

which gives us the mass susceptibility  $\chi_s$  of the solution.

From  $\chi_s$ , the susceptibility of the solute,  $\chi$ , can be easily calculated, on the basis of the additivity law

$$\chi_s = c\chi + (1-c)\chi' \quad \dots \quad (4)$$

where  $\chi'$  is the specific susceptibility of the solvent and  $c$  = the concentration of the solute in gms. per gm. of the solution.

TABLE I.

Serial number.	Substance.	<i>t</i> in °C.	<i>k</i> × 10 <sup>6</sup> .	<i>ρ</i> .	$\chi \times 10^6$ .
1.	<i>o</i> -Nitrophenol .....	47	.626	1.292	.485
2.	<i>o</i> -Nitroaniline .....	73	.632	1.259	.502
		30	.595	1.193	.499
3.	Nitrobenzene .....	{ 50.6	.587	1.173	.501
		100	.566	1.126	.502
4.	<i>m</i> -Dinitrobenzene ....	100	.554	1.355	.409
5.	<i>m</i> -Chloronitrobenzene.	48	.636	1.341	.475
6.	<i>p</i> -Dichlorobenzene ...	54	.716	1.250	.573
7.	<i>p</i> -Dibromobenzene ...	100	.786	1.830	.430
8.	<i>p</i> -Nitrotoluene .....	55	.595	1.122	.530
9.	Diphenyl.....	70	.672	0.994	.676
10.	Diphenylmethane ....	35.5	.684	0.996	.688
11.	Diphenylamine .....	55.5	.686	1.059	.648
12.	Benzophenone .....	50	.653	1.080	.604
13.	Dibenzyl .....	54.5	.671	0.964	.696
14.	Benzil .....	100	.616	1.093	.564
15.	Azobenzene .....	70.5	.611	1.042	.586
16.	<i>m</i> -Azotoluene.....	58	.643	1.057	.608
17.	Salol .....	45	.678	1.179	.575
18.	Triphenylmethane....	100	.686	1.013	.678
19.	Naphthalene .....	{ 84	.704	0.976	.721
		100	.694	0.962	.722
20.	$\alpha$ -Naphthol .....	100	.751	1.096	.685
21.	$\alpha$ -Naphthylamine ...	54	.757	1.097	.690
22.	$\alpha$ -Nitronaphthalene...	60.5	.685	1.223	.560
23.	Acenaphthene .....	100	.728	1.023	.711
24.	Fluorenone .....	100	.620	1.129	.549
25.	Phenanthrene .....	100	.764	1.063	.719

## 4. Results.

The results for the molten substances are collected together in Table I. Table II. affords a comparative

study of the gram molecular susceptibilities of the substances under different physical conditions. The single-crystal values are those of Krishnan, Guha, and Banerjee \*. The values for crystal powder are from Pascal's

TABLE II.

Substance.	Molten sub- stance.	Single crystal.	Solution.	Gm. mol. suscep. $\chi \times -10^6$ .	
					Pascal's law.
1. <i>o</i> -Nitrophenol .....	67.4	..	..	{ para- compound 67.0	66.5
2. <i>o</i> -Nitroaniline .....	69.3	{ meta- compound 69.4	..	..	70.4
3. <i>m</i> -Dinitrobenzene ....	68.7	{ para- compound 68.4	70.1 ± 1.4	66.9	67.8
4. <i>m</i> -Chloronitrobenzene.	74.7	..	..	..	78.9
5. <i>p</i> -Dichlorobenzene ...	84.2	85.4	..	..	89.3
6. <i>p</i> -Dibromobenzene ...	101.4	100.1	..	..	110.3
7. <i>p</i> -Nitrotoluene .....	72.7	..	73.1 ± .7	{ ortho- compound 72.9	72.1
8. Diphenyl.....	104.2	102.9	..	104.3	104.3
9. Diphenylmethane ....	115.5	..	..	115.2	116.0
10. Diphenylamine .....	109.5	..	..	107.3	107.1
11. Benzophenone .....	110.0	110.2	..	108.1	108.6
12. Dibenzyl .....	126.8	126.6	..	..	128.0
13. Benzil .....	118.4	114.0	114.9 ± 2.1	..	112.9
14. Azobenzene .....	106.8	104.6	..	111.4	111.4
15. <i>m</i> -Azotoluene .....	127.7	..	..	135.1	135.1
16. Salol .....	123.1	125.0	..	..	122.9
17. Triphenylmethane....	165.5	..	..	164.5	165.2
18. <i>p</i> -Benzoquinone....	..	40.0	40.6 ± 1.4	41.3	40.8
19. $\alpha$ -Naphthoquinone ..	..	73.2	70.0 ± 4.0	..	63.7
20. Naphthalene .....	92.4	93.0	93.5 ± 1.0	91.8	91.5
21. $\alpha$ -Naphthol .....	98.7	97.7	..	97.0	97.4
22. $\alpha$ -Naphthylamine ..	98.7	97.3	..	..	98.9
23. $\alpha$ -Nitronaphthalene...	97.0	..	..	97.5	97.9
24. Acenaphthene .....	109.6	108.5	109.6 ± 1.3	..	107.4
25. Fluorene .....	..	112.1	111.3 ± 1.7	110.5	110.3
26. Fluorenone .....	98.8	99.0	100 ± 2	..	102.7
27. Phenanthrene.....	128.0	128.0	129.1 ± 1.6	128.0	128.0

measurements, quoted in 'Tables Annuelles Internationales de Constantes et Données Numériques,' vol. ii. p. 386 (1913). The values given by Pascal's law are

\* The values quoted are from their latest measurements.

also taken from the same source. For a few substances for which data are not given there, they have been calculated afresh.

Nitrobenzene was studied at three different temperatures ; its susceptibility is found to be the same at all the three temperatures (see Table I.).

### 5. Conclusion.

The molecular susceptibilities given in Table II. for crystals and for molten substances are probably correct to within 1 per cent. The values deduced from the solution measurements are naturally less accurate, and the accuracy depends on the concentration of the solution and also on the amount of contraction in volume that takes place when the crystal and the solvent are mixed to give the solution. The estimated limits of accuracy of the molecular susceptibilities calculated from the solution data are indicated in the table.

It will be seen from Table II. that, within the limits of the experimental errors, *the diamagnetic susceptibility of a compound is independent of its physical state*, that is, independent of whether it is a single crystal, or is a molten liquid, or is in a state of solution.

The author wishes to express his grateful thanks to Prof. K. S. Krishnan for suggesting the problem and to Mr. S. Banerjee for much help received in the course of the work.

**XCIV. Maxwell Effect in Liquids.** *By G. G. PALDHIKAR, M.Sc., Department of Physics, D. J. Sind College, Karachi \*.*

### 1. Introduction.

**T**HAT a liquid in a state of viscous flow exhibits birefringence was first observed by Clerk Maxwell. In recent years a considerable amount of experimental work has been done on the subject, particularly by Vörlander † and his collaborators. The experimental

\* Communicated by Prof. K. S. Krishnan, D.Sc.

† Vörlander and Walter, *Zeits. Phys. Chem.* cxviii. p. 1 (1925).

arrangement used for this purpose consists of two coaxial cylinders, between which the liquid to be studied is placed. The outer cylinder is kept fixed and the inner one is rotated rapidly. A beam of light, polarized at  $45^\circ$  to the radius of the cylinders, is sent through the liquid column in a direction parallel to the axis of the cylinders, and the feeble ellipticity of the light on emergence from the liquid is measured in the usual manner with a suitable compensator.

A molecular theory of the phenomenon has been developed by Raman and Krishnan \*, based on the idea that the birefringence arises from the optical anisotropy of the molecules and their tendency to orient under the shearing stresses in the liquid, which explains satisfactorily the various features of the phenomenon. Since the publication of this paper Vörlander, Fischer, and others † have considerably improved the experimental technique, and extended the measurements to several simple liquids like benzene, the normal paraffins, etc., which, in view of our knowledge regarding the dimensions of their molecules and their optical anisotropies, are particularly suitable for a quantitative verification of the theory. An attempt is made in the present note to apply the theory to these simple liquids.

## 2. The Theory of Raman and Krishnan.

The theory is somewhat as follows. If we consider any small element of volume of the liquid in the annular space between the two cylinders the shearing stresses acting on it may be resolved into two sets of stresses, one set consisting of tensions along a direction at  $45^\circ$  to the radius and the other set consisting of pressures, of the same magnitude as the tensions, acting in a perpendicular direction. If the molecules have an elongated form they would tend to orient, under the influence of these stresses, so as to have their greatest lengths along the axis of tensions and their shorter sides along the axis of pressures. This tendency of the molecules to orient, taken together with their optical anisotropy, explains the birefringence produced.

\* Phil. Mag. v. p. 170 (1928).

† Numerous papers in *Zeits. Phys. Chem.* 1927–1932, and *Berichte*, lxxv. B, p. 1756 (1932).

We shall only quote here the final expression obtained by Raman and Krishnan for the birefringence  $n_1 - n_2$ :

$$n_1 - n_2 = \nabla \cdot \eta \cdot \frac{v}{c}, \quad \dots \dots \dots \quad (1)$$

where  $\eta$  is the coefficient of viscosity,  $v/c$  is the velocity gradient, and  $\nabla$  is a constant, called by them the Maxwell constant, given by the relation \*

$$\nabla = \frac{(n^2 - 1)(n^2 + 2)}{10n\nu kT} \cdot \Phi, \quad \dots \dots \dots \quad (2)$$

where

$$\Phi = \frac{(a_1 - a_2)(b_1 - b_2) + (a_2 - a_3)(b_2 - b_3) + (a_3 - a_1)(b_3 - b_1)}{(a_1 + a_2 + a_3)(b_1 + b_2 + b_3)}, \quad \dots \dots \quad (3)$$

$n$  is the refractive index of the liquid,  $\nu$  is the number of molecules per c.c.,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature;  $a_1$ ,  $a_2$ , and  $a_3$  are the principal dimensions of the molecule, which is treated as an ellipsoid, and  $b_1$ ,  $b_2$ , and  $b_3$  are its optical polarizabilities along these directions.

The principal dimensions of the molecules, *i.e.*, the  $a$ 's, can be obtained from X-rays or electron diffraction measurements on the molecules in the vapour state, or when such data are not available from X-ray data for the crystal state or from the known interatomic distances.

As regards the  $b$ 's, the function

$$\delta = \frac{b_1^2 + b_2^2 + b_3^2 - b_1 b_2 - b_2 b_3 - b_3 b_1}{(b_1 + b_2 + b_3)^2} \quad \dots \quad (4)$$

can be directly obtained from the depolarization factor,  $r$ , of light-scattering:

$$\delta = 5kT\beta\nu \cdot \frac{r}{6 - 7r}, \quad \dots \dots \dots \quad (5)$$

where  $\beta$  is the isothermal compressibility; the other letters have the same significance as in (2). In (3), however, the  $b$ 's do not appear in this particular combination,

\* In the original paper there was an omission, pointed out to me by Dr. Krishnan, of a factor  $1/2$  from the right-hand sides of the equations (23), (24), and (25); the work done by the tension  $\eta \cdot v/c$  in orienting the molecules, which was taken in the paper to be equal to  $\eta v/c$  multiplied by expression (22), should be only one-half of it.

and it is therefore necessary to make some simplifying assumption, *e. g.*, that the molecule has an axis of optical symmetry, before the expression for  $\Phi$  can be expressed in terms of  $\delta$ . There are two simple types of molecules for which this assumption of an axis of optical symmetry would be roughly justified : (1) benzene and its simple derivatives, for which the two polarizabilities  $b_1$  and  $b_2$  in the plane of the benzene ring may be taken to be nearly equal (and much greater than that along the normal to the plane,  $b_3$ ). For these molecules

$$\Phi = \frac{a_1 + a_2 - 2a_3}{a_1 + a_2 + a_3} \cdot \sqrt{\delta}, \dots \dots \quad (6)$$

where  $a_1$  and  $a_2$  are the two principal dimensions in the plane of the benzene ring and  $a_3$  that normal to the plane : (2) long chain molecules like the *n*-hydrocarbons of the paraffin series, for which, denoting the principal polarizabilities of the molecule perpendicular to its length by  $b_1$  and  $b_2$ , and that along the length by  $b_3$ , and the  $a$ 's along these directions by  $a_1$ ,  $a_2$ , and  $a_3$  respectively, we may put  $b_1 = b_2 < b_3$ ; the expression for  $\Phi$  for them assumes the form

$$\Phi = \frac{2a_3 - a_1 - a_2}{a_1 + a_2 + a_3} \cdot \sqrt{\delta}. \dots \dots \quad (7)$$

### 3. Application of the Theory to Aromatic Compounds.

Benzene is the simplest of these molecules. From X-ray and electron diffraction measurements \* the C-C distance may be taken as 1.41 Å., and the C-H distance as 1.14 Å., whence we obtain for benzene  $a_1 = a_2 = 6.2$  Å. The dimension perpendicular to the plane of the benzene ring is difficult to obtain directly. To a first approximation it can be obtained from the relation  $a_1 \times a_2 \times a_3 =$  average volume of the molecule in the unit cell of the crystal †

$$= 7.44 \times 9.65 \times 6.81 \text{ Å}^3/4,$$

whence we obtain

$$a_3 = 3.2 \text{ Å}.$$

\* See P. L. F. Jones, Trans. Farad. Soc. xxxi. p. 1036 (1935).

† E. G. Cox, Proc. Roy. Soc. A, cxxxv. p. 491 (1932).

For the benzene derivatives the values of the  $\alpha$ 's given in the following table have been calculated from the above data for benzene, assuming that the substituent groups are also in the plane of the benzene ring.

The densities given in the table are those of Vörlander and Fischer, and the  $\delta$ 's have been taken from Krishnan's paper \*.

The values of the Maxwell constant  $\nabla$ , calculated on the basis of expression (2), using the above data, are given in the penultimate column of Table I. The last column gives the experimental values of Vörlander and Fischer; these were obtained from the specific birefringences [D], tabulated by them, using the known dimensions of their

TABLE I.

Molecule.	Dimensions in Å.			$\rho.$	$n.$	$\sqrt{\delta}.$	$\nabla \times 10^{11}$ .	
	$a_1.$	$a_2.$	$a_3.$				Calcd.	Exptl.
Benzene .....	6.2	6.2	3.2	.881	1.502	.15	7	6
Toluene .....	7.7	,"	,"	.866	1.498	.15	8	11
Ethylbenzene .....	9.2	,"	,"	.875	1.498	.14	12	13
p-xylene .....	,"	,"	,"	.865	1.497	.16	14	26
Chlorobenzene .....	7.0	,"	,"	1.108	1.525	.17	11	16
Bromobenzene .....	7.2	,"	,"	1.497	1.560	.18	14	19
Nitrobenzene .....	8.2	,"	,"	1.206	1.553	.23	18	51
Aniline .....	7.7	,"	,"	1.025	1.586	.14	10	11
Anisol .....	9.0	,"	,"	.997	1.519	.18	14	15

apparatus (the diameters of the cylinders 185 and 184 mm.), and the known viscosity of water at 17° C. (1.09 centipoise), in terms of which as unit they have expressed the viscosities of the different liquids.

It will be seen from the table that the calculated values of  $\nabla$  are of the proper magnitude, except for nitrobenzene and xylene. Considering the various assumptions involved in the calculation this should be considered satisfactory.

Before closing this section we should mention that in cyclohexane Vörlander and Fischer could not detect any double-refraction. This is to be expected, because even assuming that the molecule is as flat as benzene,

\* Proc. Ind. Assn. Cultn. Sc. ix. p. 251 (1926).

and using the constants  $\sqrt{\delta} = .04$ ,  $\rho = .782$ , and  $n = 1.428$ , we obtain  $\nabla = 2 \times 10^{-11}$ ; actually the molecule should be more nearly spherical than benzene, so that  $\nabla$  should be much smaller than  $2 \times 10^{-11}$ , which is in agreement with observation.

#### 4. Aliphatic *n*-Hydrocarbons.

Among the normal paraffins  $C_nH_{2n+2}$  only nonicosane ( $n=29$ ) and pentatriacontane ( $n=35$ ) have been studied for their structure in some detail by Müller \* and Hengstenberg † respectively. Assuming that the earlier members,  $n=5$  to  $8$ , have also a similar structure, the lengths  $a_3$  of these molecules can be calculated, and are as given in Table II. The other two dimensions,  $a_1$  and  $a_2$ ,

TABLE II.

Molecule.	Dimensions in Å.		$\rho$ .	$n$ .	$\sqrt{\delta}$ .	$\nabla \times 10^{11}$ .	
	$a_1 = a_2$ .	$a_3$ .				Calcd.	Exptl.
<i>n</i> -Pentane	4.3	8.6	.629	1.357	.056	3	Not detectable.
Hexane	„	9.9	.690	1.376	.052	4	3
Heptane	„	11.1	.720	1.387	.048	5	Just observable.
Octane	„	12.4	.705	1.399	.047	6	4

normal to the length are more difficult to obtain. Assuming that they are equal and that the cross-sectional area,  $a_1 \times a_2$ , is the same as for nonicosane, viz.,  $18.5 \times 10^{-16}$  sq. cm., we obtain  $a_1 = a_2 = 4.3$  Å.

The calculated values of  $\nabla$  for the paraffins are given in Table II.

Here, again, the calculated values are of the proper magnitude.

Thus the experimental data support the general validity of the theory.

In conclusion, I have great pleasure in acknowledging my indebtedness to Dr. K. S. Krishnan for his helpful guidance during the course of this work.

\* Proc. Roy. Soc. A, cxx. p. 437 (1928).

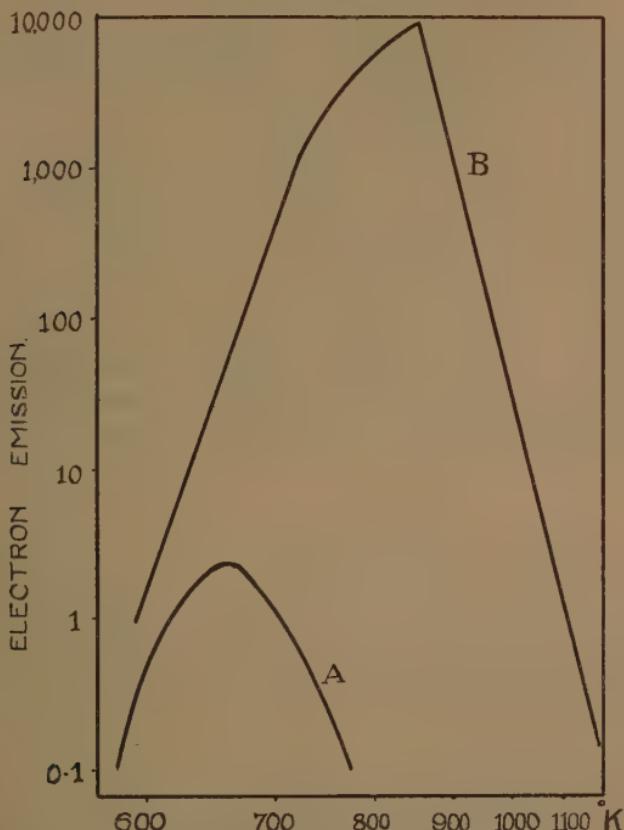
† Zeits. Krist. lxvii. p. 583 (1928).

XCV. *Cæsium-Oxygen Films on Tungsten.* By J. H. LEES,  
*Ph.D., Imperial Chemical Industries, Limited*\*.

*Introduction.*

THE properties of cæsium on oxygen on tungsten films were investigated by Langmuir and Kingdon (Proc. Roy. Soc. A, cvii. p. 61 (1925)) under various

Fig. 1.



conditions of temperature and cæsium pressure. They found that the electron emission obtainable from a tungsten surface was much increased in the presence of cæsium vapour. This increase is due to the formation of a film of cæsium on the surface of the tungsten, and it vanishes if the tungsten is heated enough to evaporate the cæsium. This is shown in fig. 1, curve A. They found, however,

\* Communicated by the Author.

that the evaporation of the caesium can be greatly reduced if the tungsten is first coated with "activated" oxygen, and the emission in that case is shown in fig. 1, curve B. This activated oxygen layer they formed by letting 0·1 mm. of oxygen for a few seconds on to the cold tungsten, pumping off, and heating the filament momentarily to a temperature of 1600° K. They found this heat treatment quite essential to obtaining the oxygen in the activated condition, but did not enquire further into the structure of the activated layer.

The experiments described in this paper were undertaken to obtain more evidence on the mode of formation of the oxygen layer, and the effect of varying the following conditions was therefore explored :—

- (a) The pressure of the oxygen forming the film.
- (b) The temperature at which the filament was activated.
- (c) The time allowed for oxygen adsorption.
- (d) The time of activation.

Owing to the departure of the author from this laboratory it has not been possible fully to complete the investigation; but it seemed worth while to present the observational material so far accumulated, as several points of some interest have already emerged.

#### *Apparatus.*

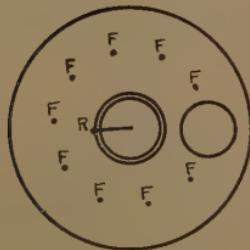
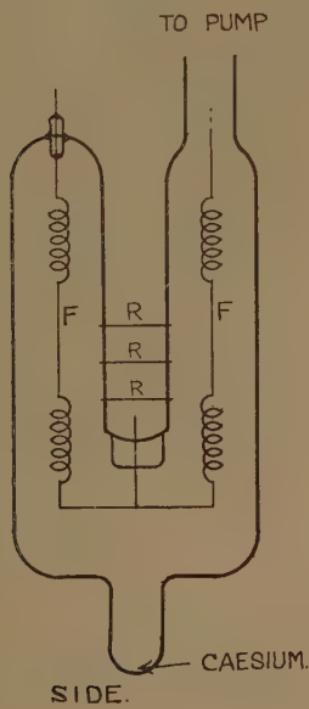
The first tube constructed consisted simply of a long filament of 0·1 mm. diameter tungsten surrounded by a collecting cylinder with guard-rings, made of nickel. The electrodes were easily outgassed by electron bombardment, and the whole tube, being of Pyrex, could be baked at 500° C.

Metallic caesium was made by heating a mixture of calcium shavings and caesium chloride to 450° C., and was distilled by stages into a bulb beneath the filament. The tube was continuously evacuated by a mercury diffusion-pump with liquid air-trap, into which the caesium very gradually distilled.

By using the filament as a surface ionization gauge (collecting cylinder negative) the caesium vapour pressure was measured, and it was at once found that the temperature of the caesium bulb was not the only factor determining the pressure. It appeared that the metal (nickel)

adsorbed large quantities of cæsium while at room-temperature, but that on heating the filament the nickel was warmed and released the adsorbed cæsium. This

Fig. 2.



PLAN.

made the cæsium vapour pressure rise considerably, and it might take as long as half an hour to fall again to the true value, whilst of course a similar spurious drop in the pressure occurred when the metal was allowed to cool. Taylor and Langmuir, in their work on cæsium

films (Phys. Rev. xliv. p. 423, 1933) experienced exactly the same trouble, and to minimize it they used as collecting electrode an evaporated platinum film upon the glass walls, so that temperature changes were kept very small.

In the final design of tube a different solution was found, as no attempt was made to keep the temperature constant, and instead the area of metal was much reduced. As will be seen in fig. 2 the electrodes are simply three wire rings, the central one for measuring the current and two outer guard rings.

Arranged symmetrically around the tube carrying these electrodes are nine tungsten filaments, each 0·1 mm. diameter and 20 cm. long, to reduce cooling at the centre due to heat loss at the ends, the greater part being coiled for compactness. The electron emission from the central centimetre of any filament is measured by making the collecting rings positive and measuring the current flowing to the central one with a galvanometer. Current saturation is not obtained with this arrangement, but as all the filaments are equally unsaturated no errors are introduced.

The great advantage of the nine-filament tube lies in the fact that every time oxygen is let into the bulb all the filaments at once are covered. This is most important, as it means that only one-ninth of the amount of oxygen necessary with previous single-filament tubes need be admitted to the nine-filament tube to get the same results. Oxidation of the caesium is thus much reduced and at the same time a good vacuum is more easily obtained. One of the filaments is generally reserved for use exclusively as a surface ionization gauge.

#### *Procedure.*

The filaments are first cleaned by flashing at 2700° K. for twenty seconds. Then the pump is cut off and a pre-determined pressure of oxygen, *e.g.*, 0·01 mm., let into the bulb for twenty seconds, after which all oxygen not adsorbed is pumped off. It was found unnecessary to freeze out the caesium vapour, as tests made with the tube immersed in liquid air showed that the presence of the vapour made no difference to the oxygen adsorption. The time required to freeze out all caesium vapour, and later to regain the full equilibrium pressure, would be

about an hour, and it will be shown later that such a delay would lead to serious errors.

Next the cæsium vapour pressure is measured, and if necessary adjusted by heating the cæsium bulb. Such heating is, however, avoided when possible, as it frequently leads to spurious results, due presumably to oxygen being released from the cæsium, or, perhaps, to cæsium oxide reaching the filaments. For this reason the cæsium is heated only if the pressure lies below 10 per cent. of the room-temperature equilibrium value, whilst for higher values the measured electron emissions are corrected to standard room-temperature cæsium pressure. From inspection of Langmuir and Kingdon's curves it appears that the electron emission is very roughly proportional to the square root of the Cs pressure, and the correction to the standard pressure was calculated on this basis. This approximation seemed amply accurate.

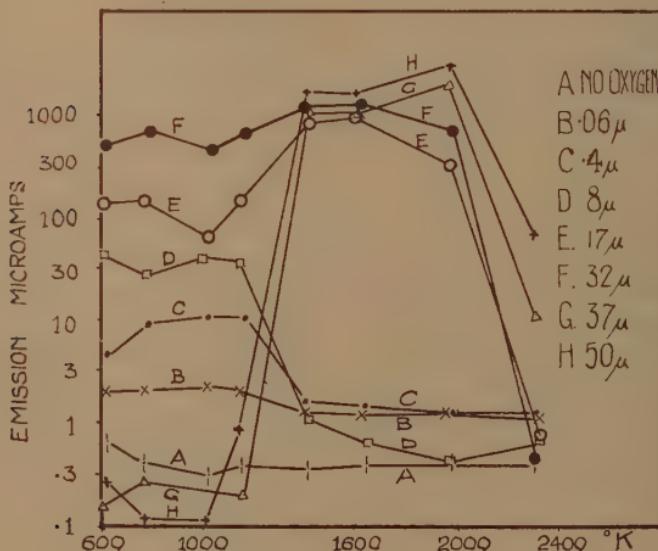
The adsorbed oxygen on the filaments is then activated by heating for a few seconds each filament to some predetermined temperature lying between 700° K. and 2300° K., after which the electron emission from each filament is measured in turn at the temperature 780° K. This gives a measure of the activated oxygen layer, as may be seen from fig. 1, and it is this electron emission which is plotted as ordinate in the figs. 3 and 4 below. An alternative measure of the activated layer would be given by measuring the emission not at the single temperature of 780° K., but over the range 600–900° K., and choosing the maximum emission obtainable. Although this would no doubt be slightly more accurate it would take a considerable time, and any delay is undesirable, as it appeared that when a perfectly clean tungsten filament was left in the best vacuum obtainable, except for cæsium vapour, its emission at the standard temperature 780° K. could not be relied upon to stay constant. This effect was very variable, as sometimes the emission would not change appreciably for days, whilst sometimes after a day it might have risen by a factor of 300. The nine filaments in this respect did not usually behave alike. Certain filaments generally showed a far greater rise than others, although all had been cut from the same reel of wire and all given the same treatment. The cause is presumably residual gas in the apparatus, and errors were minimized by taking all readings as quickly as possible.

Usually this could be done within an hour or two of flashing, and the electron emissions never altered seriously during this period.

The procedure may be summarized :—

1. Filaments cleaned by heating to 2700° K. for 20 seconds.
2. Pumps cut off and oxygen at a predetermined pressure let into the bulb for 20 seconds.
3. Cæsium pressure checked.
4. Adsorbed oxygen activated by heating the filaments momentarily to temperatures ranging between 700° K. and 2700° K.
5. Electron emission from each filament measured at the test temperature of 780° K.

Fig. 3.



### Results.

Fig. 3 shows the effect of varying the oxygen pressure and the activation temperature. Plotted as ordinate is the electron emission from each filament at the test temperature of 780° K., and as abscissa the temperature to which for 10 seconds each filament was raised for activation. It should be noted that the graph does *not* show as ordinate the emission obtained from a filament at the temperature shown as abscissa.

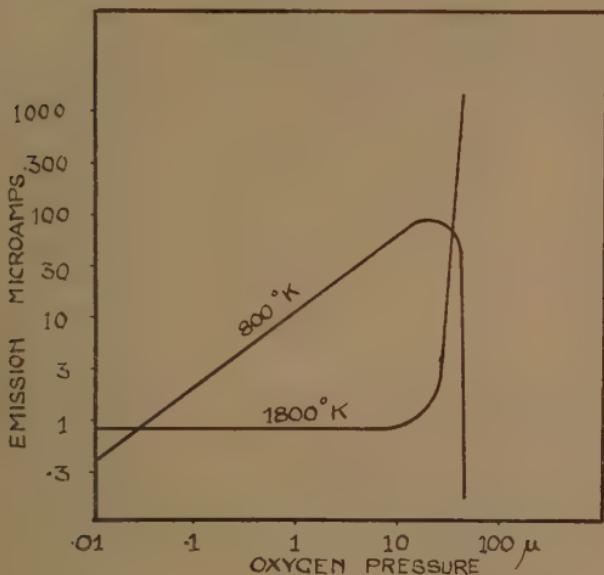
The curve A in fig. 3, representing the emission from

cæsium on clean tungsten, was obtained by going through the complete process described above, but without admission of oxygen, so that any spurious effects not due directly to the oxygen should show themselves. It will be seen that there are no such effects discernible.

The greatest emission found was obtained by letting in oxygen at high pressure and then heating the filament momentarily to  $1800^{\circ}\text{K}$ . This is precisely the procedure used by Langmuir and Kingdon.

It will be seen that the curves E, F, G, H all show reduced activation at the very highest temperature.

Fig. 4.



This is due to evaporation of the activated oxygen, which becomes appreciable at about  $2000^{\circ}\text{K}$ . and increases rapidly as the temperature rises further. Langmuir and Villars (Journ. Am. Chem. Soc. liii. p. 495) have found that the heat of evaporation is 160,000 cals./gr. atom, and using this figure calculation shows that there is a very large correction to be applied to the last point ( $2300^{\circ}\text{K}$ ) and a very small one to the next ( $1900^{\circ}\text{K}$ ). The curves are therefore shown uncorrected.

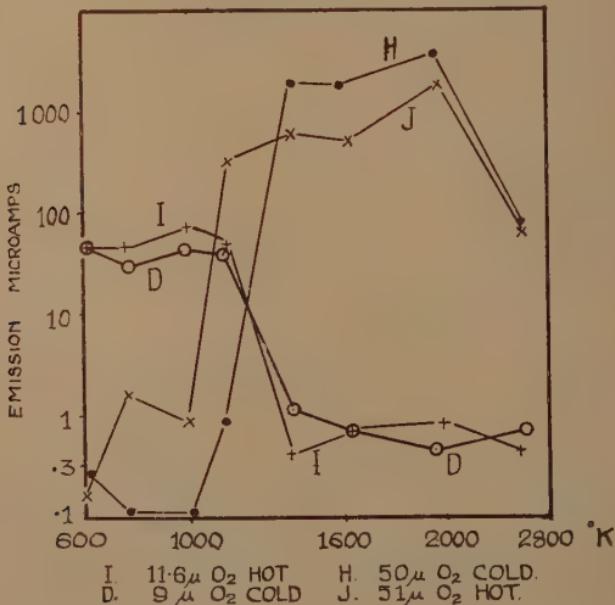
The very marked difference between the behaviour at high oxygen pressures and at low pressures is shown in different form in fig. 4. Here are plotted a typical low

temperature and a typical high temperature isotherm, instead of the isobars of fig. 3, the oxygen pressure being plotted as abscissa.

In order to test whether the critical pressure of some  $25\text{ }\mu$ , at which the character of the curves changes, is temperature dependent, the oxygen was admitted to the filaments already held at the appropriate activation temperature, the procedure being as follows :—

1. Clean all filaments by flashing for 20 seconds at  $2700^{\circ}\text{ K}$ .
2. Adjust the filament temperatures to range from  $2700^{\circ}\text{ K}$ . for the hottest to  $700^{\circ}\text{ K}$ . for the coolest.
3. Admit oxygen at a predetermined pressure to the hot filaments for 20 seconds.
4. Allow filaments to cool.
5. Measure electron emission from each filament at the standard test temperature of  $780^{\circ}\text{ K}$ .

Fig. 5.



The results, contrary to expectation, were very similar to those already described. In fig. 5 curve I was taken at  $9\text{ }\mu$  oxygen pressure, J at  $50\text{ }\mu$ . Curves D and H are the corresponding low temperature deposition curves from fig. 3, for comparison. It will be seen that at  $9\text{ }\mu$  no difference can be detected ; at  $50\text{ }\mu$  there is a definite

difference between the two curves J and H, but it seems to be of degree only as the general shapes are very similar.

Relatively few measurements were made using this second method of working, as the rate of oxidation of the tungsten was very great at the higher temperatures. Another difficulty was that the filaments had to be kept hot for a very long time until every trace of oxygen had been removed, and so when they were cooled there was the possibility of gas from the hot walls settling on the tungsten.

Nevertheless, sufficient observations were taken to establish the fact that the critical or transition pressure is temperature independent.

Some further tests were made to see if there was any effect on altering the time during which the oxygen could be adsorbed on the tungsten. In one test oxygen at a pressure of  $9\mu$  was allowed first 40 seconds for adsorption, and then 10 minutes, yet no difference was found in the activation curves. This shows that the oxygen adsorption rapidly reaches equilibrium. Nor was any effect found on altering the activation time. Usually this was 10 seconds, but if as long as 2 minutes was allowed there was no appreciable difference apart from an increased oxygen evaporation from the filaments at about  $2000^{\circ}\text{K}$ .

Finally, some preliminary observations were made which indicated a penetration of oxygen into the tungsten lattice. Thus, if an activated surface layer was removed by flashing the filament at not too high a temperature ( $<2000^{\circ}\text{K.}$ ), and the filament was subsequently held at  $<700^{\circ}\text{K.}$ , it was found that the filament gradually regained as much as 70 per cent. of its activity before flashing, while a filament to which oxygen had not been previously admitted maintained throughout the emission characteristic of clean tungsten. On the other hand, if the activated filament were flashed at, say,  $2300^{\circ}\text{K.}$  no gradual restoration of an activated surface layer was observed.

I wish to thank Dr. R. G. J. Fraser for many helpful discussions, and Professor T. M. Lowry for giving this work the ready hospitality of his laboratory.

XCVI. *The Physical Significance of Activity Coefficients in Reversible Electrode Equilibria.* By J. W. BELTON, *Physical Chemistry Department, The University, Leeds* \*.

THE application of statistical considerations to reversible electrodes has led to equations for their potential of the Nernst type<sup>(1), (2)</sup>, but difficulties have been encountered in the inclusion of the activity coefficient of the electrolyte. As the e.m.f. method is widely used for the determination of activity coefficients their significance in the electrode-solution equilibrium is of some importance. Activity coefficients have been interpreted by Gurney<sup>(2)</sup> in terms of the electric saturation of solvent molecules in the neighbourhood of ions; in the present paper it is shown how they are related to the potential of ions adsorbed at the electrode surface.

Equilibrium is established at the electrode surface when the rate at which positive ions pass from metal to solution is equal to the rate at which positive ions from the solution are neutralized. This neutralization occurs, not by direct contact, but by the transition of an electron from the metal to an ion in the vicinity, where the potential is different from that of the solution owing to the presence of an excess of ions of opposite charge near the surface of the charged electrode. Let  $V$  be the average potential difference between the region in which neutralization occurs and the electrode,  $V_1$  the potential difference between this region and the solution, and  $V_2$  that between the electrode and the solution. These potentials are related by  $V = V_1 + V_2$ . The condition for the neutralization of a positive ion for a potential difference  $V$  is

$$E_+ > \phi + V,$$

where  $\phi$  is the work function of the metal and  $E_+$  is the neutralization potential of the ion, which is defined by

$$E_+ = I_+ - W_+,$$

in which  $I_+$  is the ionization potential of the atom from which the ion is derived and  $W_+$  is its energy of hydration<sup>(3)</sup>.

\* Communicated by the Author.

The number of ions neutralized per unit area of the electrode surface in unit time is given by

$$n_2 = N_2 A_2 e^{-(\phi + V)/kT}, \dots \quad (1)$$

where  $N_2 = \sqrt{RT/2\pi M}$ ,  $M$  is the weight of a gram-ion, and  $A_2$  is the number of positive ions per c.c. of solution. In order to leave the surface ions must possess an energy greater than some value  $\psi$  depending on their vibrational energy in the lattice. All ions of energy greater than  $\psi + \phi$  are neutralized; the number escaping from the metal per unit area in unit time is thus

$$n_1 = \int_{\psi}^{\psi + \phi} A_1 e^{-E/kT} dE, \dots \quad (2)$$

which will depend only on the metal. At equilibrium  $n_1 = n_2$ , and hence

$$V = -\phi + \frac{RT}{nF} \log \frac{A_2}{n_1} N_2$$

and  $V_2 = -\phi + \frac{RT}{nF} \log \frac{A_2}{n_1} N_2 e^{-V_1/kT}. \dots \quad (3)$

The e.m.f. of a cell has been shown by Fowler<sup>(4)</sup> to be given by

$$E = C + V'' + V', \dots \quad (4)$$

in which  $C$  is the contact potential between the two electrodes and  $V'$  and  $V''$  are the interface potentials, which are given by (3). Substitution gives

$$\begin{aligned} E = \pi'' - \pi' &= \frac{RT}{nF} \log \frac{A_2''}{n_1''} N_2'' e^{-V_1''/kT} \\ &\quad - \frac{RT}{nF} \log \frac{A_2'}{n_1'} N_2' e^{-V_1'/kT}. \end{aligned} \quad . \quad (5)$$

Here  $\pi''$  and  $\pi'$  refer to the separate electrode potentials, that is, the potentials when combined with a normal hydrogen electrode. For a concentration cell  $A_2'' = A_2'$  and  $n_1'' = n_1'$ ; hence

$$E = V'' - V' = \frac{RT}{nF} \log \frac{N_2'' e^{-V_1''/kT}}{N_2' e^{-V_1'/kT}} = \frac{RT}{nF} \log \frac{f'' N_2''}{f' N_2'}, \quad (6)$$

which is the well-known logarithmic expression, where the activity coefficient of the electrolyte is given by

$$f = e^{-V_1/kT}. \quad . \quad . \quad . \quad . \quad (7)$$

An approximate evaluation of (2) further shows that the normal electrode potential is related to the thermionic work function.

Equation (7) gives a relation between the activity coefficient of the electrolyte and  $V_1$  which for convenience may be termed the adsorption potential. The surface of the charged electrode may be regarded as a lattice of positive ions all of which are not neutralized. These positive ions are surrounded on the liquid side of the interface by an ion atmosphere of opposite sign which forms the adsorbed layer. The potential due to such a hemispherical atmosphere is given by the Debye-Hückel theory as

$$-\frac{\epsilon k}{2D},$$

and the work done in bringing an ion of charge  $\epsilon$  up to it is  $\epsilon^2 \kappa / 2D$ , which is equal to  $V_2$  for a univalent ion. Hence from (7)

$$\log f = -\frac{\epsilon^2 \kappa}{2DKT},$$

which is the Debye-Hückel equation for the activity coefficient of an electrolyte.

This view of the adsorbed layer is true only for very dilute solutions. The treatment of concentrated solutions is difficult, but the following comparison is interesting. The potential  $V_1$  is dependent on the number of ions adsorbed which is given by the adsorption isotherm derived by Pinkus and Brouckère<sup>(5)</sup> for the adsorption of ions on a crystalline surface,

$$x = \frac{c}{Af(c) + Bc},$$

where  $x$  is the amount of electrolyte adsorbed,  $A$  and  $B$  are constants, and  $f(c)$  some function of  $c$  the concentration of the electrolyte. Thus  $V_1$  is given by

$$V_1 = \frac{c}{A'f'(c) + B'c}$$

and

$$-\log f = \frac{c}{[A'f'(c) + B'c]kT},$$

which is of the same form as the Debye-Hückel equation for moderately concentrated solutions

$$-\log f = \frac{A\sqrt{c}}{1+B\sqrt{c}}$$

if  $f(c)$  can be approximately written as a square root.

Numerical values of the adsorption potential may be calculated from equation (7) from known activity coefficients; no data are available for this potential for direct comparison, but the calculated values are of a reasonable order of magnitude, as is shown by the following table :—

Adsorption Potentials corresponding to  
Activity Coefficients.

$f.$	V (volts).
0.9	0.77
0.8	1.63
0.7	2.60
0.6	3.73

These potentials all correspond to less than a unimolecular layer of ions. Assuming a layer at a distance from the metal of molecular dimensions, the number of excess ions which will give a potential of one volt is of the order  $3 \times 10^{13}$  per unit area. A unimolecular layer could accommodate perhaps a hundred times this number.

In conclusion, it should be pointed out that the activity coefficient of an electrolyte is usually regarded as an intrinsic property of the solution, while in the above discussion it is treated as a property of the interface. From the thermodynamic point of view the activity coefficient gives a measure of the deviation of the behaviour of a real solution from that of an ideal solution, but in practice the methods used for the determination of activity coefficients—freezing-point depression, elevation of the boiling-point, vapour pressure, solubility—all involve a phase equilibrium and are amenable to treatment similar to that given above.

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 (4) Fowler, Trans. Farad. Soc. xxviii. p. 369 (1932).  
 (5) Pinkus and Brouckère, J. Phys. Chem. xxv. p. 605 (1928);  
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### XCVII. *Notices respecting New Books.*

*Introduction to Quantum Mechanics.* By LINUS PAULING and E. BRIGHT WILSON. [Pp. xiii+468.] (New York and London : McGraw-Hill, 1935. Price 30s.)

THIS book is concerned essentially with the Schrödinger equation and the problems which can be treated by means of it. After a brief survey of classical mechanics and the old quantum theory the equation is applied to the harmonic oscillator, the point particle in three dimensions, and the hydrogen atom. Perturbation theory is dealt with fully, and the variation and other approximate methods are described. An account of the spinning electron and the Pauli exclusion principle leads to a discussion of many-electron atoms. There are three chapters on molecules, with an interpolated chapter on perturbation theory involving the time, and the resonance phenomenon. Miscellaneous applications of wave mechanics are briefly considered, and there is a final short chapter on the general theory of quantum mechanics.

Most of the topics considered have been dealt with before in one or other of the now numerous books on quantum mechanics. In none of these books, however, has the particular field been covered with such a wealth of expository detail. It is this which gives the book its particular value. Many, if not most, of the students of physics (using the term student in its widest sense) are unfamiliar with the details of the mathematical technique required in the development and application of the Schrödinger equation, and the most striking characteristic of many of the treatments of particular problems appears to be the number of gaps in the argument. Pauling and Wilson fill in these gaps.

The book is intended for readers with no extensive previous experience of advanced mathematics, and it is written with thorough appreciation of the requirements of such readers. Clearness of exposition is attained not by simplification of the problems considered but by full explanations of the various steps in the detailed treatment. The book provides an admirable guide to those physicists and chemists who wish to gain a practical working knowledge of wave mechanics, and it may be warmly commended.

*Mathematics and the Question of the Cosmic Mind.* By C. J. KEYSER. [Pp. vi+121.] (*Scripta Mathematica*, New York, 1935. Price 75 cents.)

OF the six essays in this booklet by the Adrian Professor Emeritus of Mathematics at Columbia University, the first three constitute a logical sequence dealing with the nature and bearing of mathematics. The view developed is that the basic subject matter of mathematics consists of propositional functions; and that mathematical propositions are essentially established hypothetical propositions, answering questions about the logically possible. Mathematics is contrasted with science, of which the aim is to establish categorical propositions about the actual world. It is held that the domain of mathematics is much more extensive than that of number and space, though it is in dealing with number and space that the most famous and elaborate applications of mathematics have been made. Attention is directed to the value of the mathematical way of thinking, both directly and as a pattern, in connexion with the "major concerns of man." It is concluded, in the title essay, that the universe may rightly be said to be a realm of mind in virtue of the logical structure discoverable in it.

In the fourth essay a plea is made for the cultivation of the art of democratizing the higher forms of knowledge as a means of "mitigating the tragedy of our modern culture"; and a number of popular expositions of modern science are sympathetically criticized. A discussion of the study of legal science illustrates the utility of the mathematical method, and the book closes with an appreciation of the many-sided mathematician, William Benjamin Smith.

There is much worth saying and well said in these essays. The reader must, however, discount occasional idiosyncrasies of phraseology. The character of these is sufficiently indicated by the fact that one of the author's books, often referred to here, which deals with the realm of mathematics and science, is entitled '*Pastures of Wonder*'.

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[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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